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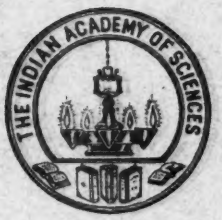

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AN OPTICAL METHOD OF DETERMINING THE RELATIVE COAGULATING POWERS OF ELECTROLYTES.

By Ch. V. Jogarao.
(From the Department of Physics, Andhra University, Waltair.)

Received February 25, 1937.
(Communicated by Mr. S. Bhagavantam.)

1. Introduction.

The relative coagulating powers of electrolytes can be obtained by taking the reciprocals of their respective flocculation values. The flocculation values for a number of electrolytes have been determined by Freundlich and others by finding out the smallest concentrations of the electrolyte required to produce complete coagulation in a given time. The progress of coagulation of colloids by electrolytes has also been studied and followed by different workers by different methods. D. N. Ghosh (1932) measured the intensity of the scattered light by means of a Nutting Colorimeter and obtained therefrom the order in which the flocculation values of some monovalent and bivalent chlorides decrease. Joshi and Narayan Lal (1933) followed the progress of coagulation of a manganese sol by measuring the surface tension of the coagulating sol by means of the stalagmometer. Joshi and Viswanath (1933) studied the coagulation of arsenic sulphide sol by observing the viscosity changes during the progress of coagulation. An outstanding inference of all these workers is that, in general, coagulation is a continuous process. In this paper, it is proposed to apply a recently discovered optical method for following up the coagulation of arsenic sulphide sol by different electrolytes. The results enable us to obtain the order in which the coagulating powers of the different electrolytes decrease.

2. Description of the Method.

Based upon Mie's theory of the scattering of light by large particles, R. S. Krishnan (1934) has developed a new optical method of obtaining relative estimates of the size and shape of the scattering particles. The method consists in measuring the depolarisation factors of the scattered light using alternately horizantally polarised and vertically polarised incident light. The terms ρ_u, ρ_v and ρ_h occurring hereafter signify respectively, the depolarisation of the scattered light when the incident light is unpolarised, when it

is vertically polarised and when it is horizontally polarised. In this paper the depolarisation is always expressed as the ratio of the intensity of the weak component to that of the strong component irrespective of whether the horizontal component is weaker or stronger than the vertical component. The experimental arrangements used are the same as those described by the author in a previous investigation (Jogarao, 1936).

The significance of the measurements is as follows. Any departure from unit value for ρ_h indicates a finite size for the scattering particle, *i.e.*, a size large when compared with the wavelength of light. Any departure from zero value for ρ_v indicates that the scattering particles are not spherical. ρ_u is related to ρ_v and ρ_h in a simple manner (Krishnan, 1934). So if the values of ρ_h and ρ_v are observed for the light scattered by the coagulating sol at regular intervals during the progress of coagulation, we get relative estimates of the size and shape of the particles of the coagulating sol at different instants of time. Coagulation is only a process involving the colloidal particles adhering together into larger groups as a result of their electric charge being neutralised by the oppositely charged particles of the electrolyte or the coagulator. We should therefore expect the value of ρ_h to decrease gradually as coagulation proceeds until the coagulation is complete. Thereafter ρ_h should remain more or less constant.

Subbaramayya (1935) used this method for showing that the size of the colloidal particle increases with time, in the case of a number of sols. In this paper it is proposed to study the arsenic sulphide sol not only from the point of view of the progress of coagulation but also with a view to determine the relative efficiencies of various coagulators.

3. Arsenic Sulphide Sol in Neutral and Acid Media.

A preliminary investigation relating to the coagulation of arsenic sulphide sol in an acid medium is described in this section. Arsenic sulphide sol is prepared in a neutral medium in the following manner :—

0·03 g. of arsenious acid are dissolved in 200 c.c. of conductivity water and hydrogen sulphide is passed into it. Excess of hydrogen sulphide is afterwards driven out by bubbling hydrogen through it, until the sol is free from hydrogen sulphide.

Two cubical glass cells are made and cleaned and washed with conductivity water. 30 c.c. of the sol are put in each of them. 3 c.c. of dilute hydrocholric acid of known concentration are added to one of the cells. ρ_h and ρ_v are measured at intervals of 4 to 5 hours with both cells, *i.e.*, for the sol in a neutral medium and for the sol in an acid medium.

The results are represented in Tables I and II.

TABLE I.

ρ_h and ρ_v for Arsenic Sulphide Sol in an Acid Medium.

Concentration of the sol : 0·75 millimols per litre. Concentration of the acid : 75 millimols per litre.

Time	Just before adding acid	Just after adding acid	After 3 hours	After 6 hours	After 9 hours	After 13 hours	After 19 hours	After 20 hours	After 23 hours	After 25 hours	After 2 days	After 3 days
ρ_h ..	·671	·671	·195	·200	·117	·097	·059	·052	·050	·047	·045	·045
ρ_v ..	·003	·003	·003	·003	·003	·003	·003	·003	·003	·003	·003	·003

TABLE II.

ρ_h and ρ_v for Arsenic Sulphide Sol in a Neutral Medium.

Concentration of the sol : 0·75 millimols per litre.

Time	First Reading	After 3 hours	After 9 hours	After 13 hours	After 19 hours	After 23 hours	After 2 days
ρ_h	·671	·648	·648	·648	·648	·648	·648
ρ_v	·003	·003	·003	·003	·003	·003	·003

The important conclusions from the results of this preliminary investigation are :—

1. Coagulation proceeds continuously in the acid medium as is indicated by the decreasing value of ρ_h in Table I.

2. Coagulation does not take place in the neutral medium as is indicated by a more or less constant value for ρ_h in Table II.

3. In the acid medium coagulation proceeds very rapidly at first and slowly thereafter.

4. The colloidal particles are very nearly spherical and continue to be so throughout as is indicated by the extremely small and constant value for ρ_v.

These results are in agreement with the observations of previous workers.

4. *Application of the Method for Determining the Relative Coagulating Powers of Electrolytes.*

Nine glass bulbs, each having a capacity of about 15 c.c., are made and well cleaned and washed finally with conductivity water. Arsenic sulphide

sol is prepared again in neutral medium as described in the foregoing section. Solutions are made of known concentrations of nine electrolytes, namely, the chlorides of potassium, sodium, ammonium, barium, calcium, strontium, aluminium and iron and hydrochloric acid. 5 c.c. of the electrolyte solution are added to 10 c.c. of the sol thus making up a total volume of 15 c.c. in each bulb. ρ_h is measured for each bulb at intervals of an hour, until it attains a constant value. The results obtained are given below.

TABLE III.

Electrolytes containing Monovalent Cations.

Concentration of the sol: 0·5 millimols per litre. Concentration of the electrolyte: 33 millimols per litre.

Electrolyte	Just before adding electrolyte	Just after adding electrolyte	After 1 hour	After 2 hours	After 3 hours	After 4 hours	After 5 hours	After 6 hours	After 7 hours	After 8 hours	After 9 hours	After 10 hours
HCl ..	·467	·467	·390	·307	·320	·283	·238	·248	·246	·259	·254	·250
NH_4Cl ..	·444	·444	·365	·275	·240	·214	·236	·252	·178	·219	·181	·219
KCl ..	·448	·448	·357	·214	·258	·246	·235	·179	·175	·190	·204	·190
NaCl ..	·435	·435	·440	·415	·402	·336	·335	·287	·226	·252	·252	·247

TABLE IV.

Elecrtolytes containing Bivalent Cations.

Concentration of the sol: 0·5 millimols per litre. Concentration of the electrolyte: 0·33 millimols per litre.

Electrolyte	Just before adding electrolyte	Just after adding electrolyte	After 1 hour	After 2 hours	After 3 hours	After 4 hours	After 5 hours	After 6 hours	After 7 hours	After 8 hours	After 9 hours
$CaCl_2$ ..	·464	·464	·283	·208	·194	·163	·147	·147	·139	·143	·147
$SrCl_2$ ..	.438	·438	·390	·259	·208	·194	·194	·155	·159	·158	·158
$BaCl_2$ ..	·422	·422	·472	·301	·327	·213	·203	.180	·155	·158	·158

TABLE V.

Electrolytes containing Trivalent Cations.

Concentration of the sol: 0·5 millimols per litre.

Concentration of the electrolyte: 0·015 millimols per litre.

Electrolyte	Just before adding electrolyte	Just after adding electrolyte	After 1 hour	After 2 hours	After 3 hours	After 4 hours	After 5 hours	After 6 hours
$FeCl_3$	·448	·187	·034	·034	..	..	..	..
$AlCl_3$	·448	·207	·191	·155	·132	·081	·081	·079

5. Discussion of Results.

In Figs. 1 and 2, smooth curves showing the progressive variation of ρ_h with time are given. The concentrations given at the top of the Tables III, IV and V show that the concentrations of the electrolyte in the case of the trivalent cation is much smaller than in the case of the divalent cation which in its turn is much smaller than in the case of the monovalent cation. In spite of this, complete coagulation occurs in a shorter time in the case of the trivalent cations, than in the case of the divalent cations. In the latter case again complete coagulation occurs in a much shorter time than in the case of the monovalent cations. This shows that the coagulating power of the trivalent cations is much greater than that of the bivalent cations and that of the bivalent cations is much greater than that of the monovalent cations. This result is in agreement with the well-known results of Freundlich and others.

Fig. 1 shows that in the case of the four monovalent chlorides, the coagulating powers are in the order $HCl > NH_4Cl > KCl > NaCl$.

This result is obtained from the fact that a steady value of ρ_h is reached earliest for HCl, next for NH_4Cl, next for KCl and lastly for NaCl.

Similarly Fig. 2 shows that in the case of the three bivalent chlorides the coagulating powers fall off in the order $CaCl_2 > SrCl_2 > BaCl_2$.

In the case of the two trivalent chlorides, the order is

$$FeCl_3 > AlCl_3.$$

These results may be seen to be the same as those derivable from the flocculation values given by Ghosh, Freundlich and others.

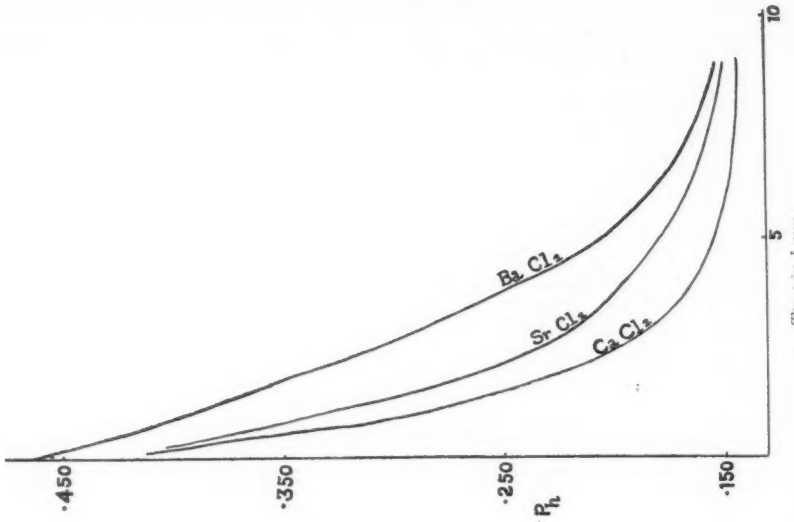
Ba Cl2
Sr Cl2
Ca Cl2
·450
·350
·250
·150
Rh
5
10
Time in hours

Fig. 2.

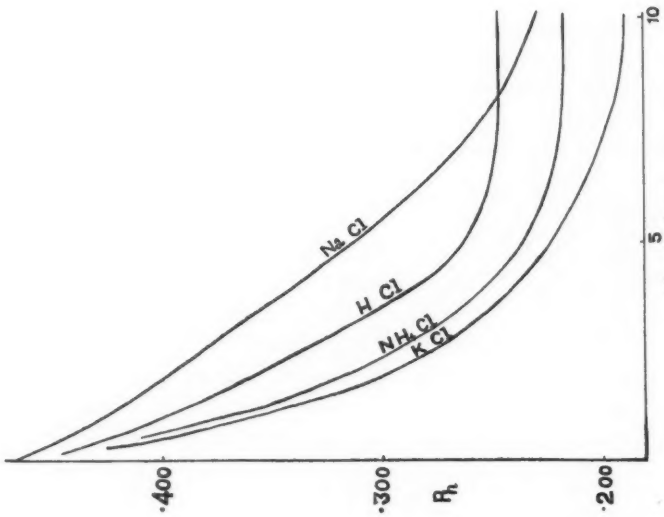
Na Cl
H Cl
NH4 Cl
K Cl
·400
·300
·200
Rh
5
10
Time in hours

Fig. 1.

Another important result which comes out of the present investigation is that, the concentration of the sol remaining the same, the ultimate size of the colloidal particle differs for different coagulators. In the case of the monovalent chlorides the steady value of ρ_h is of the order of about 0·25. In the case of the bivalent chlorides it is about 0·15 and in the case of the trivalent chlorides it is about 0·05. These figures indicate that the particle grows to a much larger size when the coagulator contains a trivalent cation than when it cantains a divalent or a monovalent cation.

6. *Summary.*

The progress of coagulation of arsenic sulphide sol has been followed by means of an optical method. By applying this method, the relative coagulating powers of nine electrolytes, namely, chlorides of potassium, sodium, ammonium, barium, strontium, calcium, aluminium and iron and hydrochloric acid have been determined. The conclusions drawn are as follows.—The coagulating powers of the monovalent chlorides are in the order $HCl > NH_4Cl > KCl > NaCl$, those of the bivalent chlorides are as $CaCl_2 > SrCl_2 > BaCl_2$ and those of the trivalent chlorides are as $FeIC_3 > AlCl_3$. It is also concluded that the final size reached by the colloidal particle as a result of coagulation depends upon the valency of the cation of the coagulator. In the case of the trivalent cations the final size of the colloidal particle is larger than that obtained in the case of the bivalent and the monovalent cations.

The author takes this opportunity of expressing his gratefulness to Mr. S. Bhagvantam, Head of the Physics Department, for his valuable guidance during the course of this investigation.

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THE RAMAN SPECTRA OF CRYSTAL POWDERS.

IV. Some Organic and Inorganic Compounds.

By R. Ananthakrishnan.

(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received February 22, 1937.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

In several previous communications, the author has pointed out that the new technique of complementary filters described by him has opened out for the study of Raman effect an extensive array of crystalline compounds in the domain of organic as well as of inorganic chemistry whose investigation by the method of light-scattering has till now remained extremely meagre, incomplete or inadequate for reasons of a technical nature. The procedure sometimes adopted in such cases, of studying the substance in solution or in the molten state, has several limitations, and is attended with difficulties, into which it is not necessary to enter at great length. Suffice it to remark that, as the first two papers of this series have made it clear, profound spectral changes—even the complete washing out of the entire spectrum—can and sometimes do occur when a substance is dissolved in water. Again, in the case of a large number of crystalline solids of high melting point, prolonged maintenance of the substance above this temperature during the exposure causes partial or total decomposition of the substance itself, a difficulty which has been already pointed out by Kohlrausch (1936). These difficulties are all overcome by the powder technique, and in favourable cases, comparison of the Raman spectrum of the solid substance with the spectrum of the same substance in solution or in the molten state, can be expected to furnish important conclusions. The present paper is an attempt in this direction, and embodies the results of the author's investigation on the Raman spectra of crystalline naphthalene, oxalic acid, urea, guanidine hydrochloride, acetamide, propionamide, amino-acetic acid, phenyl acetic acid, phosphorous acid, sodium phosphite, phosphoric acid and boric acid.

2. *Experimental.*

All the crystalline solids were Kahlbaum's purest chemicals, and were mostly used directly without any preliminary treatment. A Hilger two-prism spectrograph of high light-gathering power and a Fuess spectrograph of somewhat larger dispersion than the Hilger instrument were employed to photograph the Raman spectra. The duration of exposure varied with the nature of the substance, and was minimum in the case of naphthalene which yielded a very intense spectrum on the Hilger instrument in about 10 hours. λ 4046 was the exciting line in all cases.

3. *Results.*

The results are contained in Table I. The notations employed have the following significance :

t = time of exposure in hours ; n = total number of observed lines.

F = Fuess spectrograph ; H = Hilger two-prism spectrograph.

TABLE I.

1. *Naphthalene*, $t = 10$; $n = 18$; H	511 3s	764 5s	1019 5s	1144 3s	1168 1s	1240 2s	1280 ½	1328? 0	1379 15s	1440 1s	1460 5s	1573 7s	1623 ½s	3001 1s	3025 0	3054 12s	
2. *Oxalic acid*, $(COOH)_2 \cdot 2H_2O$ $t = 70$; $n = 5$; H	485 0s	854 6s	1360 ½	1486 2d		3432 6	3467 4bd										
3. *Urea*, $OC(NH_2)_2$ $t = 72$, $n = 10$; H	1012 10s	1171 ½d	1465 ½d	1537 2	1576 ½		3243 2d	3324 4d	3353 5d	3434 5							
4. *Guanidine Hydrochloride*, $\left[HN=C\begin{matrix}NH_2\\NH_2\end{matrix}\right]\cdot HCl$ $t = 72$; $n = 10$; F	526 0	1006 10s	1554 5	1624 0d		3172 1d	3238 1d	3279 1d	3338 4d	3430 1d							
5. *Acetamide*, $H_3C \cdot CO \cdot NH_2$ $t = 40$; $n = 13$; H	455 1s	875 8s	1147 5s	1354 3	1397 3d	1594 1d		2933 10s	2970 0d	3020 0d	3150 6bd	3286 1d	3351 4d				
6. *Propionamide*, $H_5C_2 \cdot CO \cdot NH_2$ $t = 48$; $n = 12$; H	820 4s	1145 5s	1418 2d	1456 2d	1594 1d		2743 ½d	2850? 0	2897 3s	2942 8s	2997 4s	3173 4bd	3356 3bd				
7. *Amino-acetic acid*, $H_2N \cdot CH_2 \cdot COOH$ $t = 48$; $n = 17$; H	507 1	893 5s	1047 2s	1121 1s	1132 ½d	1319 4d	1336 6d	1397 4b	1437 4s	1499 1bd	1577 1d	1650 ½d	2592 ½d	2870 1d	2959 10	2999 8s	3113 3bd

8. *Phenyl acetic acid*, $C_6H_5 \cdot CH_2 \cdot COOH$ $t = 48$; $n = 20$; F	624 1s	748 3s	840 4s	890 ½	925 ½d	1003 10s	1032 6s	1188 4s	1234 3	1338 1	1402 1	1432 ½d	1585 2	1600 3	2920 6	2952 1	2986 ½	3013 ½	3035 ½	3063 12
9. *Phosphorous acid*, H_3PO_3 $t = 12$; $n = 6$; H	961 6s	990 3d	1038 2	1104 1d			2485 8s	2511 7s												
10. *Sodium phosphite*, Na_2HPO_3 $t = 72$; $n = 4$; H	969 3s		1046 1	1057 1			2338 6s													
11. *Phosphoric acid*, H_3PO_4 $t = 24$; $n = 2$; H	919 10s	1100 (?) 1d																		
12. *Boric acid*, $B(OH)_3$ $t = 70$; $n = 3$; F	880 5s		3172 3d	3256 2d																

4. *Discussion of Results.*

1. *Naphthalene.* The Raman spectrum of naphthalene in the crystalline state was reported by Bär (1929) in his very first communication in which he pointed out the possibility of obtaining Raman spectra with crystal powders instead of single crystals. The spectrum of the molten substance has been studied by Petrikaln and Hochberg (1929), Ziemecki (1932), and Gockel (1935); Dadieu and Kohlrausch (1929) have photographed the spectrum of the solution of naphthalene in CCl_4. It is of interest to compare the results of the previous authors with the frequencies recorded in the present investigation. Table II gives such a comparison.

TABLE II.

Dadieu and Kohl. (1929) Soln. in CCl_4	Petrikaln and Hoch. (1929) molten	Ziemecki (1932) molten	Gockel (1935) molten	Bär (1929) Cryst.	Author (1937) Cryst.
505 (2)	516 (4)	511 (3)	512(5)	514	511 (3s)
610 (0)	..	..	..	..	..
..	..	742 (2)	..	..	..
..	762 (4)	763 (3)	761 (5)	761	764 (5s)
936 (0)	..	..	..	..	..
1023 (2)	1029 (4)	1026 (3)	1026 (4)	1025	1019 (5s)
1142 (0)	1157 (1)	..	1153 (½)	..	1144 (3s)
..	..	..	..	..	1168* (1s)
1245 (0)	..	..	1251 (0)	..	1240 (2s)
..	1293 (4) ?	..	..	..	1280* (½)
..	..	1323 (0)	1323 (1)	..	1328 (0) ?
1377 (4)	1381 (5)	1377 (10)	1379 (8)	1391	1379 (15s)
1412 (0)	..	..	..	..	..
..	..	..	..	..	1440* (1s)
..	1463 (3)	1460 (4)	1462 (4)	..	1460 (5s)
1573 (3)	1580 (3)	1575 (4)	1572 (3)	..	1573 (7s)
..	..	..	..	..	1623* (½s)
..	..	..	..	..	3001* (1s)
..	..	..	..	..	3025* (0)
3046 (1b)	3064 (4)	3058 (4)	3062 (4b)	3068	3054 (12s)

* Frequencies noticed for the first time.

An inspection of the table reveals at once that many new frequencies have been recorded in the spectrum of this substance. Comparison of the author's results with those of Bär shows the vast improvement effected by the technique of complementary filters in the photography of the Raman spectra of crystal powders. A characteristic feature of the Raman spectrum of naphthalene crystals is the extreme sharpness of all the modified lines. Some difference between the spectra of the substance in the solid and molten states is noticed in the region of the hydrogen frequencies above 3000 cm.$^{-1}$ In the crystals, three sharp lines are present in this region, while Gockel and others have found only a single broad line in

the spectrum of molten naphthalene. This difference is very significant in the case of a non-polar substance, because it shows that the hydrogen frequencies are very susceptible to temperature and the state of aggregation of the substance even in such cases. Influence of change of state and presumably also of temperature on the C–H frequencies was noticed by the author (1936) in the case of cyclopropane, and recently Bhagavantam and Rao (1937) observed intensity and frequency changes for the hydrogen lines of benzene on passing from the liquid to the vapour state. The 1379 line of naphthalene is the most intense line in the whole spectrum, and does not seem to undergo any appreciable change on passing from the solid to the molten state. It might be of interest to note that it is also a very prominent line in the spectra of the α- and β- mono-derivatives of naphthalene.

2. *Oxalic Acid,* $(COOH)_2 \cdot 2H_2O$. Rao (1935), Hibben (1935) and Angus and Leckie (1936) have examined the Raman spectrum of crystalline oxalic acid. Aqueous solutions of the acid have also been studied by the above authors and more recently by Gupta (1936). Some controversy appears to have arisen between Hibben on the one hand and Angus and Leckie on the other as to the presence or otherwise of frequencies near 1700 cm.$^{-1}$ corresponding to C = O in the Raman spectrum of oxalic acid dihydrate. Unfortunately, as only λ 4046 excitation was employed in the present investigation, frequencies in the 1700 region, even if present, could not have been observed because of the presence of the λ 4358 group of mercury lines. Comparison of the Raman frequencies of oxalic acid dihydrate observed by the author with those reported by Hibben and Angus and Leckie is given below :—

TABLE III.

Hibben		847	1365	1470				
Angus and Leckie	495	854		1471	1661(b)	1759		
Author	485 0	854 6s	1360 ½	1486 2d			3432 6	3467 4bd

The frequencies of crystalline oxalic acid reported in a recent paper by Balmokand Anand (1936) appear to be entirely false. A new feature of the present investigation is that it shows the presence of two strong Raman frequencies in the 3400 region which presumably originate from the oscillations of the water molecules.

3. *Urea*, $OC.(NH_2)_2$. The Raman spectrum of this substance has been studied in the aqueous solution by Pal and Sen Gupta (1930), Krishnamurti (1931), Kohlrausch and Pongratz (1934), and recently by Edsall (1936). Krishnamurti also studied the Raman spectrum of the crystalline substance by the powder technique and recorded two frequencies 1006 (strong) and 1134 (weak). The broad water-band in the 3 μ region renders the complete elucidation of the N–H frequencies which fall practically in the same region very difficult indeed in the case of aqueous solutions, and it is, therefore, of interest to compare the spectrum of the crystalline substance recorded by the author with the previous results on aqueous solutions.

TABLE IV.

Kohlrausch and Pongratz (aq. soln.)	525 2b	585 1b	1000 8	1157 1b	1350 ½	1458 0		1593 2b	1665 0		3218 1b	3383 3vb	3462 2vb
Edsall (aq. soln.)	521 1	584 1	1000 6	1170 1vb		1468 0		1580 0	1666 1b	1768 ?	3230 1	3380 3b	3489 1b
Author (crystal)			1012 10s	1171 ½d		1465 ½d	1537 2	1576 ½		3243 2d	3324 4d	3353 5d	3434 5

It is seen that the frequency near 1000 cm.$^{-1}$ is the most prominent one in the crystal as well as in the aqueous solution. Its magnitude shows a distinct diminution on passing from the crystal to the aqueous solution, a feature which has been also noticed by Krishnamurti. A significant difference between the spectrum of the crystal and of the solution is the absence in the latter of the frequency near 1537 cm.$^{-1}$ which is a very prominent line in the crystal spectrum, and which probably arises from a δ (N–H) oscillation. Differences seem to exist even in the region of the N–H valence oscillations, as can be seen from Table IV. These differences are, of course, due to the large influence of the highly polar solvent on the solute molecules. Failure to observe the frequencies in the 500 and 1700 region in the crystal spectrum does not mean their non-existence.

The usually written chemical formula of urea is $O = C\begin{matrix}NH_2\\NH_2\end{matrix}$. If we regard the C, O and N atoms as being in the same plane, the molecule has the symmetry C_{2v}. On this basis, Kohlrausch and Pongratz have attempted to discuss the spectrum of this substance by comparing it with the Raman spectra of presumably similar molecules such as acetone,

$O=C\begin{matrix}CH_3\\CH_3\end{matrix}$ and phosgene, $O=C\begin{matrix}Cl\\Cl\end{matrix}$. Nevertheless, as far as the present author can see, the resemblance between the spectra of these substances in the spectral region concerned (below 1800 cm.$^{-1}$) is by no means of a very striking character, and polarisation measurements are necessary before any definite classification of the frequencies can be attempted.

Krishnamurti has suggested the possibility that urea might exist in two tautomeric forms :

$$O=C\begin{matrix}NH_2\\NH_2\end{matrix} \rightleftharpoons HO-C\begin{matrix}NH\\NH_2\end{matrix}$$

However, it appears very difficult to decide this issue by the evidence furnished by the Raman spectrum of urea.

During the last few years, Pauling and his collaborators have attacked the problem of the nature of chemical valence from the standpoint of the quantum theory, and have published a series of interesting papers in which they have adduced very strong evidence in favour of resonance between the various possible configurations in the case of those molecules in which the normal electronic state can be represented by more than one Lewis structure. According to Pauling's view (1935), resonance exists in the case of urea between the three alternative structures,

$$O=C\begin{matrix}NH_2\\NH_2\end{matrix} \rightleftharpoons \bar{O}-C\begin{matrix}\overset{+}{N}H_2\\NH_2\end{matrix} \rightleftharpoons \bar{O}-C\begin{matrix}NH_2\\\overset{+}{N}H_2\end{matrix}$$

(i) (ii) (iii)

the resonance being of sufficient importance to give each C–N bond 28 per-cent double bond character. The influence of such resonance on the Raman spectrum of the molecule concerned is rather a complicated problem ; nevertheless, if we are justified in regarding the simultaneous existence of the two different types of molecules represented by (i) and (ii), [forms (ii) and (iii) are not essentially different] we might expect to find certain characteristic features in the region of the N–H valence frequencies. In a previous paper (1937) the author pointed out that a change in the co-valency of nitrogen from three to four causes an appreciable diminution of the N–H frequencies. Kohlrausch (1936) has tabulated the N–H valence frequencies observed in the Raman spectra of a series of primary amines of the type $R\cdot N\begin{matrix}H\\H\end{matrix}$ and has found the mean values 3313 and 3367 cm.$^{-1}$ for the two

frequencies observed in this region. The departure from the mean values does not exceed 10 or 15 wavenumbers in individaul cases. The author's previous investigations showed that the N–H frequencies of the ions $[NH_4]^+$, $[H_3N \cdot OH]^+$ and $[H_3N \cdot NH_3]^{++}$ observed in the Raman spectra of their crystalline salts are well below the values given above, and extend over the spectral range 2500–3200 wavenumbers. If we are to accept the Pauling resonance structure of urea, it is probable that the bands 3243 (2*d*) and 3324(4*d*) owe their origin primarily to the $=\overset{+}{N}H_2$ group, and the bands 3353(5*d*), 3434(5) primarily to the $-NH_2$ group. The increase above the normal values of these frequencies could then be attributed to the influence of the resonating double bond.

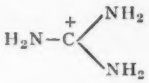
4. *Guanidine Hydrochloride,* $\left[HN = C\begin{matrix}NH_2\\NH_2\end{matrix}\right] \cdot HCl$. The Raman spectrum of the guanidonium ion in aqueous solutions of its salts has formed the subject-matter of a recent investigation by Gupta (1936). The spectrum of the aqueous solution obtained by him and that of the crystalline salt reported in the present investigation differ in certain important respects as can be seen from the following table.

TABLE V.

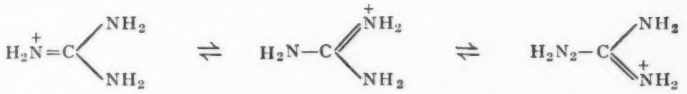
Gupta (aq. soln.)	522 1	995 4		1620 ½b					
Author (crystal)	526 0	1006 10s	1554 5	1624 0d	3172 1d	3238 1d	3279 1d	3338 4d	3430 1d

Besides showing a large number of frequencies in the N–H region, the spectrum of the crystalline salt exhibits a strong line at 1554 cm.$^{-1}$ which is absent in the aqueous solution. We notice, moreover, a definite fall in the frequency of the most intense Raman line near 1000 cm.$^{-1}$ on dissolving the substance in water. In these respects, there is a very close similarity between the guanidonium ion and urea. It is also very significant that the frequency of the strongest Raman line is practically the same in the two cases.

The structure of the guanidonium ion has been discussed by Theilacker (1931, 1935) in connection of his X-ray investigation of the crystal structure of the guanidonium halides. His results show that from the crystallographic standpoint, all the three nitrogen atoms of the guanidonium ion are equivalent. This result is, however, insufficient to decide between the two alternative structures of this ion :

(i) the non-resonating structure 

(ii) the resonating structure



Theilacker has concluded in favour of the formula (i), while Pauling and Sherman (1933) postulate for the guanidonium ion a double bonded resonance structure with three-fold degeneracy as is shown by formula (ii).

Gupta has stated that the low value of the strongest Raman frequency of the guanidonium ion, *viz.*, 1000 cm.$^{-1}$ rules out the possibility of the Pauling double-bond resonance structure and lends every support to the Theilacker non-resonating structure. The present author, however, fails to see the force of this argument because, as has been already pointed out, we find an identical and equally intense frequency in the spectrum of urea the molecule of which certainly contains a double bond. On the other hand, if we bear in mind that the masses of NH_2 and O are identical, and that the C–N and C–O force constants are not appreciably different, the Pauling resonance structure enables us at once to understand the close coincidence of the frequencies observed in the Raman spectrum of the guanidonium ion and of urea. The N–H frequencies in the 3000 region are of interest in this connection. We find N–H frequencies greater and less than 3300 wavenumbers in the spectrum of guanidine hydrochloride. This is probably an indication of the presence of $=\overset{+}{N}H_2$ as well as of $-NH_2$ groups in the guanidonium ion. In any case, the arguments adduced by Gupta in favour of the symmetric non-resonating model of the ion—the low value of the frequency of the strongest Raman line, and its high degree of polarisation—are not sufficient to rule out the Pauling structure.

The strong Raman frequency at 1554 cm.$^{-1}$ in the crystal which is apparently non-existent in the solution represents probably a δ (N–H) frequency. Disappearance of such sharp and intense δ (N–H) frequencies in aqueous solutions has been noticed by the author in the case of hydroxylamine and hydrazine hydrochlorides. The reason for this is not clear.

5. *Acetamide, $H_3C \cdot CO \cdot NH_2$.* The Raman spectrum of this substance is of great interest because the phenomenon of resonance predicted by Pauling and Sherman (1933) in the case of amides appears to have been confirmed from several different sources such as the measurement of dipole

moment (by Kumler and Porter, 1934), from the magnetic susceptibility (by Clow and Thompson, 1936), etc., and some evidence for the same might be expected from the Raman spectrum. In the case of acetamide, the expected resonance is between the structures

As far as the author is aware, the Raman spectrum of acetamide has not been examined in the crystalline state. The spectrum of the molten substance has been studied by Kohlrausch and Pongratz (1934) and by Thatte and Joglekar (1935). As the results of the latter authors are incomplete, we shall not consider them here. Kohlrausch and Pongratz have found the surprising result that the Raman frequencies characteristic of the NH_2 group are completely absent in the spectrum of this substance. In this and other respects, the author's results on the Raman spectrum of acetamide crystals forms a striking contrast as can be seen from Table VI.

TABLE VI.

Kohlrausch and Pongratz (molten, 92°)	236 0	448 3	564 3	862 7b	1119 3b	1344 3b	1387 3b	1422 ½	1611 2	1660 ± 9 3b		2933 6b	2998 2
Author (crystal)	..	455 1s	..	875 8s	1147 5s	1354 3	1397 3d	..	1594 1d	..		2933 10s	2970 0d
									3020 0d	3150 6b		3286 1d	3351 4d

The absence of the N–H frequencies in the molten substance, if genuine, is indeed very significant, in view of the fact that they come out quite strongly in the crystals; the matter, however, requires re-examination. The N–H frequencies of the solid consist of three diffuse bands of which the one of lower frequency at 3150 is more intense than the others of higher frequency. In acetamide, if we are to postulate the co-existence of two types of molecules in equal proportion, then, excepting in the region of the N–H frequencies, we cannot expect any appreciable differences between the vibrational frequencies of the two forms, since the vibrating masses and the force constants concerned are nearly identical. For reasons which have been already explained, it seems justifiable to attribute the N–H band at 3150 to

the $R\cdot C\begin{matrix}O\\ \\ {}^{+}NH_2\end{matrix}$ type and the bands of higher frequency to the $R\cdot C\begin{matrix}O\\ \\ NH_2\end{matrix}$ type of molecules.

Kohlrausch and Pongratz have suggested the possible occurrence of the tautomeric forms $R\cdot C\begin{matrix}O\\ \\ NH_2\end{matrix}$ and $R.C\begin{matrix}OH\\ \\ NH\end{matrix}$ in acetamide, on the ground that two Raman frequencies are observed in the 1600 region instead of one (see Table VI).

6. *Propionamide*, $H_5C_2\cdot CO\cdot NH_2$. The crystals employed were somewhat fluorescent and hence the spectrum showed an appreciable background. Even so, the N–H frequencies in the 3000 region were very clearly recorded, the spectrum differing in this respect from that reported by Kohlrausch and Pongratz (1934) for the molten substance.

TABLE VII.

Kohlrausch and Pongratz (molten, 80°)	269 2b	453 3b	555 2b	807 8b	997 3b	1056 3b	1131 4b	1244 2b	1291 1	1413 4b
	1453 4b	1606 2b	1664 ± 13 4b		1691 2	2848 2	2913 5	2942 5b		
Author (crystal)	820 4s	1145 5s	1418 5s	1594 1d	2742 ½d	2850? 0	2897 3s	2942 8s	3173 4d	3356 3d

The N–H bands are practically in the same position as in acetamide, and suggest resonance of a similar nature in this case also. The agreement between the C–H frequencies of the solid with those of the molten substance is fairly good, although their relative intensities seem to be somewhat different in the two states.

7. *Amino-acetic acid* (*Glycocoll*), $H_2N\cdot CH_2\cdot COOH$. This is the simplest member of a homologous series of acids characterised by very exceptional properties. All the compounds of this series belong to the so-called class of *amphoteric electrolytes*, *i.e.*, substances that possess both basic and acidic properties. Study of the dielectric constants of aqueous solutions of these acids has furnished the most crucial evidence in favour of the view originally put forth by Bjerrum (1922) that the aliphatic-amino-acids in the undissociated state exist practically entirely as salt-like " zwitter ions " or dipolar ions, $\overset{+}{N}H_3\cdot R\cdot COO^{-}$. They are therefore characterised by the

possession of large permanent electric moments. According to Bjerrum, the amino-acids are far from being acids in the usual sense of the term; they are more correctly pictured as ammonium salts.

When an amino-acid is dissolved in water, the reactions taking place are as follows:

$$\overset{+}{N}H_3 \cdot R \cdot COO^- \rightleftharpoons NH_2 \cdot RCOO^- + H^+$$

$$\overset{+}{N}H_3 \cdot RCOO^- + H^+ \rightleftharpoons \overset{+}{N}H_3 \cdot R \cdot COOH$$

We see that the acid character of the amino-acid is supplied by the substituted ammonium group, while the carboxyl end of the molecule is responsible for its basic nature.

Because of the many interesting properties of the amino-acids outlined above, their Raman spectra in the solid state and as aqueous solutions are of great interest. Some results in this connection have been published recently by Edsall (1936). He has studied a number of amino-acids in aqueous solution, and has found that in all cases the characteristic carbonyl group frequency in the 1700 region is absent in them. The corresponding frequency, however, appeared strongly in the spectra of aqueous solutions of the hydrochlorides of all the amino-acids studied by him. From this Edsall has concluded that the carbonyl group $-C\begin{matrix}=O\\ \diagdown OH\end{matrix}$ is absent in the free acid, which shows that neutral amino-acids in aqueous solution exist as "zwitter ions" $\overset{+}{N}H_3 \cdot R \cdot COO^-$. The hydrochlorides, on the other hand, have the configuration $\overset{-}{Cl} \cdot \overset{+}{N}H_3 \cdot R \cdot COOH$ so that the carbonyl group frequency comes out in the spectra of the amino-acid cations. Edsall has also examined the Raman spectrum of amino-acetic acid in the crystalline state; his results do not show any striking difference between the spectrum of the crystals and that of the aqueous solution.

In a more recent communication, Kahovec and Kohlrausch (1936) have reported the Raman spectra of the aqueous solution and crystals of amino-acetic acid. They have found certain discrepancies between their results and those of Edsall. It is therefore of interest to compare the results obtained in the present investigation with the frequencies observed by the previous workers.

TABLE VIII.

Aqueous solution		Crystalline		
Edsall	Kahovec and Kohlrausch	Edsall	Kahovec and Kohlrausch	Author
..	236 (0)	..	..	..
508 (2b)	498 (1)	507 (½)	..	507 (1)
590 (1)	587 (1)	598 (1)	..	..
665 (1)	709 (½)	..	..	..
..	800 (0)	..	..	..
897 (3)	891 (2)	891 (2)	870 (4)	893 (5s)
1033 (1)	1029 (2)	1033 (1)	1020 (2)	1047 (2s)
1122 (1)	1099 (3)	1112 (½)	1130 (2)	1121 (1s)
				1132 (½d)
..	1210 (0)	..	..	..
1331 (3)	1348 (3)	1323 (3)	1320 (7)	1319 (4d)
				1336 (6d)
1412 (3)	1407 (3b)	1404 (3)	1400 (4)	1397 (4b)
1491 (0)	..	1436 (3)	1440 (2)	1437 (4s)
..	..	..	1510 (1)	1499 (1bd)
..	..	..	1570 (1)	1577 (1d)
1630 (1vb)	1624 (½) (doublet)	..	1650 (½)	1650 (½d)
..	..	..	..	2592 (½d)
..	..	..	..	2870 (1d)
2978 (3b)	2972 (00)	2968 (3)	2960 (3)	2959 (10)
3018 (1)	..	3002 (1)	..	2999 (8s)
..	..	..	..	3113 (3bd)

Table VIII brings out a number of interesting features. In the first place, we see that the crystal frequencies reported previously are very incomplete indeed. Kahovec and Kohlrausch explained the discrepancy between their results and those of Edsall by pointing out the extreme difficulty of obtaining good photographs of the Raman spectra of crystal powders. The technique of complementary filters completely overcomes all these difficulties, and it is therefore not surprising that both in the matter of the relative intensities of the lines as well as in their total number, the author's results differ from those of Edsall and of Kohlrausch.

Edsall in a recent note (1936) on the Raman spectra of amines and methylated ammonium ions, has pointed out that while the free primary and secondary amines $R \cdot NH_2$ and $RR' \cdot NH$ give one or two intense Raman lines between 3300 and 3400 cm.$^{-1}$, presumably associated with the unionised N–H bond, the corresponding ammonium chlorides $[R \cdot NH_3]^+ Cl^-$, $[RR' \cdot NH_2]^+ Cl^-$, $[RR'R'' \cdot NH]^+ Cl^-$ in which the amino group has acquired a proton show no Raman frequencies above 3050 cm.$^{-1}$ He appears to have arrived at this conclusion by the study of the spectra of the aqueous solutions of the chlorides. Conversely, he has concluded that since the isoelectric

amino-acids show no Raman frequencies above 3030 cm.$^{-1}$, it clearly follows that the amino group in these acids is electrically charged.

As has been already explained, the author found from a study of the spectra of the crystalline salts of ammonium, hydroxylamine and hydrazine that the N–H frequencies observed in these compounds in which the covalency of nitrogen is four, are much lower compared with the N–H frequencies observed in the amines wherein nitrogen is trivalent. The N–H frequencies of crystalline amino-acetic acid are of interest in this connection. The three diffuse bands 2592($\frac{1}{2}d$), 2870($1d$) and 3133($3bd$) observed in the spectrum of this substance are presumably N–H frequencies, and fall within the limit (2500 to 3200 cm.$^{-1}$) of the N–H frequencies formerly observed by the author in the case of compounds in which the covalency of nitroge is four. *This is therefore positive evidence that there is no free amino group in crystalline amino-acetic acid, and that the constitution of the free acid is* $H_3\overset{+}{N}\cdot CH_2\cdot COO^-$.

The failure of Edsall and of Kahovec and Kohlrausch to observe any of the above N–H frequencies in the spectrum of crystalline amino-acetic acid is in all probability due to the inferior quality of the powder photographs obtained by them. On the other hand, the absence of the N–H frequenices in aqueous solutions of this acid is of significance. In a series of papers Freymann and Freymann (1936) have recently reported the interesting result of what they call ' the dissimulation of the N–H frequencies in the case of tetra-covalent nitrogen compounds '. From their investigation of the Raman spectra as well as the near infra-red absorption spectra of aqueous solutions of a number of nitrogen compounds, these authors arrived at the very general conclusion that the N–H frequencies in the 3 μ region, while quite intense in all those compounds wherein nitrogen is three-covalent, are completely absent in all those compounds in which nitrogen is four-covalent. They also pointed out that on account of the quite general nature of this result, the presence or absence of the 3 μ N–H bands in a nitrogen compound can be expected to furnish important information regarding its constitution. These conclusions are practically identical with those of Edsall.

We have, however, to bear in mind the important fact noticed by the present author, that the N–H frequencies are actually lowered from their normal values in the primary and secondary amines, in the tetra-covalent nitrogen compounds. In a previous paper (1937) the author also remarked that these lowered frequencies in four-covalent nitrogen compounds are considerably weakened or otherwise perturbed in aqueous solutions. Their

complete disappearance is a point about which the author is not quite certain. Freymann and Freymann assume the entire dissappearance of the N–H frequencies in aqueous solutions of four-covalent nitrogen compounds such as NH_4Cl, and postulate that this result can probably be only explained by assuming that the N–H bonds which are covalent in the crystalline state, become electrovalent in solution. This is a point which the author shall not go into in the present commuuication. It might be of interest to point out that the frequency 1577 observed in the crystal is absent in the aqueous solution. This is presumably a δ (N–H) frequency.

8. *Phenyl acetic acid, $C_6H_5 \cdot CH_2 \cdot COOH$.* As far as the author is aware, the Raman spectrum of this substance has been studied only by Kohlrausch and Pongratz (1934). These authors have reported the spectrum of the molten substance, which agrees reasonably well with the author's frequencies for the crystalline solid.

TABLE IX.

Kohlrausch and Pongratz (molten)	245 3b	470 2	616 4	751 4	845 4	893 1b	—	998 10	1029 4	1161 1	1188 4	—	—
Author (crystal)	—	—	624 1s	748 3s	840 4s	890 ½	925 ½d	1003 10s	1032 6s	—	1188 4s	1234 3	1338 1
Kohlrausch and Pongratz	1400 1b	—	1593 6b	1662 ± 7 1b			2924 1	—	2981 0	—		—	3055 3
Author	1402 1	1432 ½d	1585 2	1600 3			2920 6	2952 1	2986 ½	3013 ½	3035 ½	3063 12	

However, many new frequencies have been observed in the solid spectrum, and we notice also remarkable differences between the spectra of the solid and molten substance in the region of the hydrogen frequencies. This emphasises once again the susceptibility of the hydrogen frequencies to external influences such as change of state, temperature, etc., which is presumably much more pronounced here on account of the polar nature of the substance.

9, 10. *Phosphorous acid and Sodium phosphite, H_3PO_3 and Na_2HPO_3.* The information furnished by the Raman spectra of these two substances relating to the question of the constitution of phosphorous acid and the phosphites, has already been briefly reported by the author in a recent note in *Nature* (1936). Before going into the question in somewhat greater detail

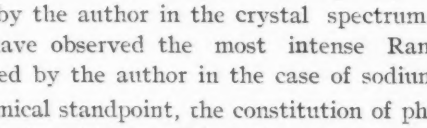
it might be of interest to compare the author's results on the Raman spectra of these two substances with the frequencies observed by Ghosh and Das (1932) for the corresponding aqueous solutions.

TABLE X.

Ghosh and Das (H_3PO_3 aq.)	672 5b	940 4	1012 2				
Author (H_3PO_3 crystal)		961 6s	990 3d	1038 2	1104 1d	2485 8s	2511 7s
Ghosh and Das (Na_2HPO_3 aq.)		978 3		1030 1			
Author (Na_2HPO_3 crystal)		961 3s		1046 1	1057 1	2338 6s	

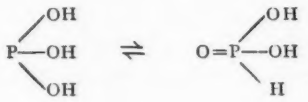
The strong Raman frequency 672(5*b*) reported by the latter authors in the spectrum of H_3PO_3 solution is most probably incorrect since there is not even a trace of it in the spectrum of the crystalline acid. The author is inclined to believe that there is a mistake in the assignment of Ghosh and Das in the case of this line. The wavenumber as reported by them is 22265, and if the line is assumed to originate from λ 4046 excitation instead of λ 4358 as these authors suppose, the corresponding frequency shift works out as $\Delta\nu = 2440$ cm.$^{-1}$, which is near the frequency shift of the Raman doublet observed by the author in the crystal spectrum. Ghosh and Das do not seem to have observed the most intense Raman frequency at 2338 cm.$^{-1}$ observed by the author in the case of sodium phosphite.

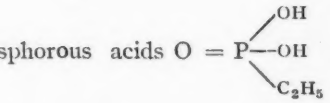
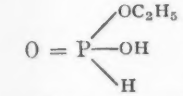
From the chemical standpoint, the constitution of phosphorous acid has been a long-disputed problem. This is because of the rather conflicting nature of the chemical evidence in this case. The mode of formation of the acid from PCl_3 and water as represented by the equation



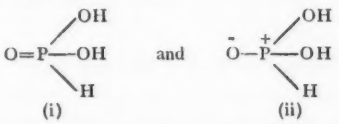
suggests that the acid is tri-basic, and that all the three -OH groups are identically linked to the phosphorus atom. Nevertheless, it has been known from long since that the acid is only dibasic, *i.e.*, only two atoms of hydrogen can be replaced by metals to form salts (NaH_2PO_3 and Na_2HPO_3). In order to explain this apparent anomaly, it has been generally assumed that

in the process of formation of the acid from PCl_3 and H_2O, it undergoes the tautomeric change



While the existence of two ethyl phosphorous acids  and  supports the asymmetric formula of the acid, normal esters of phosphorous acids of the type $P(OC_2H_5)_3$ are also known, which can be adduced as evidence in favour of the symmetric form.

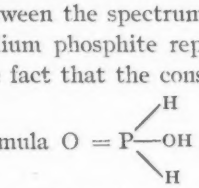
The Raman spectra of phosphorous acid and sodium phosphite furnish valuable evidence regarding the constitution of the acid. In both these compounds, Raman frequencies are observed in the 2400 region, which can presumably arise only from a P–H oscillation. Thus, *the presence of a P–H linkage in phosphorous acid is definitely established, so that the symmetric configuration of the acid has to be ruled out.* We have only to decide between the two alternative Lewis structures



(i) (ii)

It is probable that formula (i) gives the correct picture. According to Pauling (1933), the molecules of oxygen acids can be represented as containing either covalent bonds or ionic bonds, and their properties are best understood by considering both the extreme cases. Pauling has also remarked that the ionic extreme can be considered to be more closely approached in the case of those oxygen acids in which the highest valency of the element comes into play such as H_2SO_4, H_3PO_4, etc., while in oxygen acids of elements in their lower valency states such as H_3PO_3, H_2SO_3, etc., the covalent character of the bonds is more pronounced. The present investigation, however, clearly shows that phosphorus in H_3PO_3 is certainly in its highest valency state.

Recently, Redlich, Kurz and Stricks (1936) have examined the Raman spectrum of the hypophosphite ion $(H_2PO_2)^-$ in aqueous solutions of sodium hypophosphite. Unfortunately, the author has been unable to see

their original paper, but from the brief summary of their results in *Physikalische Berichte* (1936, **17**, 2075), there appears to exist some similarity between the spectrum of this ion with the spectra of phosphorous acid and sodium phosphite reported in the present paper. This is probably due to the fact that the constitution of hypophosphorous acid is represented by the formula  . Two frequencies 2358(4*b*) and 2450(1) have been observed by the above authors in the spectrum of the hypophosphite ion, which indicates the existence of two P–H linkages. While only one Raman line is observed in the 2400 region in the spectrum of sodium phosphite, a sharp and well-separated doublet appears in the spectrum of crystalline phosphorous acid. Since these compounds contain only one P–H linkage, this can only mean that the P–H frequency is split up in the case of the acid.

11. *Phosphoric acid*, H_3PO_4. The crystalline acid was badly fluorescent so that the spectrum showed an intense background. Only two Raman lines could be distinguished whose frequency shifts are given in Table I. In the case of the 1100 frequency, there is a partial superposition of the Raman line 919 due to λ 4078 excitation. Since the spectrum of this acid has been discussed previously by various authors, it is not necessary to consider it any further.

12. *Boric acid*, $B(OH)_3$. The Raman spectrum of an aqueous solution of boric acid was examined by the author on a former occasion ; because of the intense fluorescence, only one frequency 875 cm.$^{-1}$ could be identified. The spectrum of the crystalline acid shows in addition to this line two rather diffuse bands at 3172 and 3256 cm.$^{-1}$, presumably arising from the O–H oscillations. This is of interest in connection with a recent paper of Bernal and Megaw (1935) dealing with the function of hydrogen in intermolecular forces. They have distinguished between two kinds of bonds between hydrogen and oxygen, the *hydrogen bond* and the *hydroxyl bond*. In oxy-acids of the type $XO_n(OH)_m$, *e.g.*, H_2SO_4, the bond between O and H is the hydrogen bond so that the hydrogen ion can migrate to a neighbouring oxygen atom. This possibility of migration does not exist in hydroxy-acids of the type $X(OH)_n$, so that the bond in such cases is a hydroxyl bond. The above authors have pointed out the absence of the O–H frequency in Raman spectra of the acids of the former type as evidence for the presence of the hydrogen bond in them. They have also remarked that hydroxyl bonds should be present in crystalline boric acid ; the present investigation

confirms this view. It is, however, noteworthy that the O–H frequencies observed in this case are somewhat lower than those generally observed in the alkali hydroxides.

In conclusion, the author's grateful thanks are due to Professor Sir C. V. Raman for his kind interest in the present work.

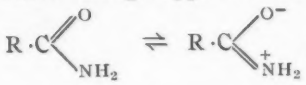
Summary.

Employing the technique of complementary filters recently described by the author, the Raman spectra of naphthalene, oxalic acid dihydrate, urea, guanidine hydrochloride, acetamide, propionamide, amino-acetic acid, phenyl acetic acid, phosphorous acid, sodium phosphite, phosphoric acid, and boric acid have been studied in the crystalline state. The results are discussed at some length in relation to the work of previous investigators on the Raman spectra of these compounds in solution or in the molten state. Naphthalene crystals give an intense spectrum consisting of very sharp lines. Many new frequencies have been observed in the spectrum of the crystals. The crystal spectrum shows certain differences in the region of the C–H frequencies when compared with the spectrum of molten naphthalene. Two strong bands in the 3400 region have been recorded in the spectrum of oxalic acid dihydrate in addition to the frequencies hitherto reported for this substance. These bands are due to the O–H oscillation of the water molecules.

The spectrum of crystalline urea shows certain characteristic differences when compared with the spectrum of its aqueous solution. An intense sharp line at 1012 cm.$^{-1}$ in the crystal shifts to 1000 cm.$^{-1}$ in the solution. A frequency at 1537 which is strong in the crystal spectrum is absent in the spectrum of the aqueous solution. Since disappearance of such sharp and intense lines in this frequency region has been formerly noticed by the author in the case of the crystalline salts of hydroxylamine and hydrazine on dissolving them in water, it is concluded that this is a δ(N–H) frequency. The N–H valence frequencies of crystalline urea consist of four bands 3243(2*d*), 3324(4*d*), 3353(5*d*) and 3434(5). The spectrum of the guanidonium ion in guanidine hydrochloride crystals shows a close similarity with the spectrum of urea. The intense Raman line at 1006 cm.$^{-1}$ in the crystal shifts to 995 cm.$^{-1}$ in solution. A strong frequency 1554(5) in the crystal apparently disappears on dissolving the substance in water. This is therefore considered as a δ(N–H) frequency. The N–H valence frequencies in the crystal consist of a number of bands extending from 3170 to 3430 wavenumbers. It is pointed out that the Pauling double bond resonance

structure of urea and the guanidonium ion enables one to understand the observed similarity between their spectra.

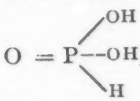
The N–H frequencies are strongly recorded in the spectra of crystalline acetamide and propionamide. This is an interesting result in view of the fact that Kohlrausch and Pongratz have reported the complete absence of N–H frequencies in the Raman spectra of these amides in the molten state. The N–H frequencies are practically identical in the spectra of acetamide and propionamide, and consist mainly of two intense bands 3150(6*b*), and 3350(4*b*). While the frequency shift of the second band falls in the region of the N–H frequencies observed in the case of primary and secondary amines, the frequency of the first one is much less, and falls in the frequency interval (2005 to 3200 cm.$^{-1}$) of the N–H frequencies observed by the author in the tetra-covalent nitrogen compounds. It is pointed out that this fact lends strong support to the resonance structure in the case of amides



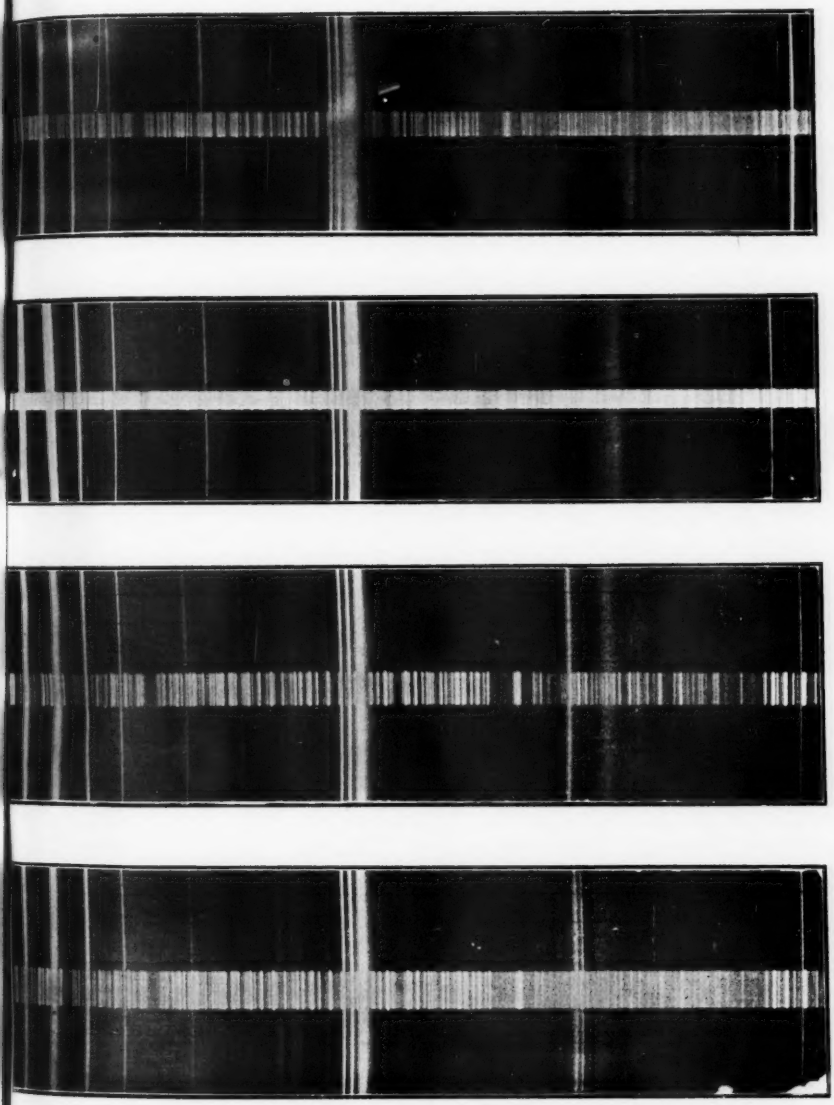
postulated by Pauling.

The spectrum of crystalline amino-acetic acid reported here differs in certain important respects from the spectra of the crystalline acid and its aqueous solution reported by previous investigators. No N–H frequencies are observed in the 3300 region in the spectrum of this substance, but three diffuse bands 2592($\frac{1}{2}d$), 2870(1*d*), 3113(3*d*) are observed in the spectrum of the crystalline acid, which presumably arise from N–H oscillations. This shows that nitrogen is tetra-covalent in crystalline amino-acetic acid, and hence that the molecules of the crystalline acid exist as " zwitter ions " (Bjerrum), $\overset{+}{N}H_3 \cdot CH_2 \cdot COO^-$ —a result amply confirmed from various other sources.

Phosphorous acid and sodium phosphite show P–H frequencies in the 2400 region, from which it is concluded that the constitution of the acid is



, the maximum valency of phosphorus coming into operation. In contrast to the numerous oxy-acids, boric acid shows O–H frequencies in the 3200 region. This confirms the view of Bernal and Megaw that the bonds between O and H in acids of the former type are hydrogen bonds, while in hydroxy-acids such as $B(OH)_3$, hydroxyl bonds are present.



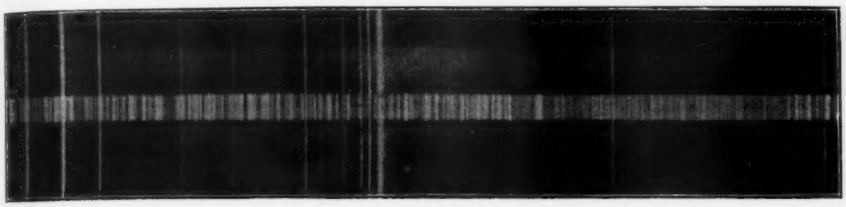
Urea
$OC \cdot (NH_2)_2$

Guanidine hydrochloride
$\left[HN{=}C\begin{matrix}NH_2\\NH_2\end{matrix}\right] \cdot HCl$

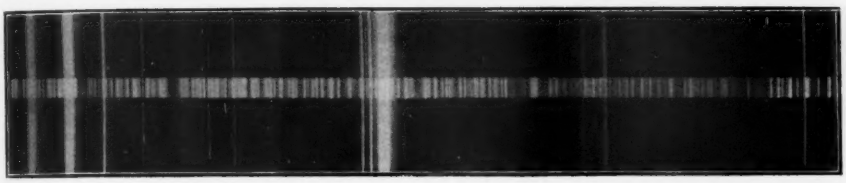
Acetamide
$H_3C \cdot CO \cdot NH_2$

Glycocoll
$H_2N \cdot CH_2 \cdot COOH$

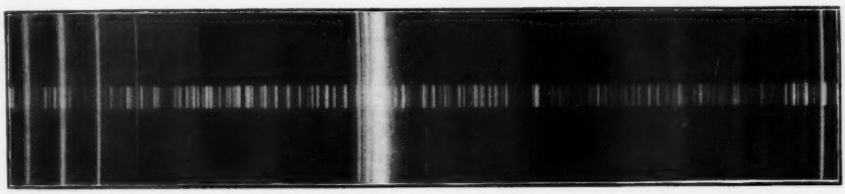
FIG. 1. Raman Spectra of Crystal Powders.



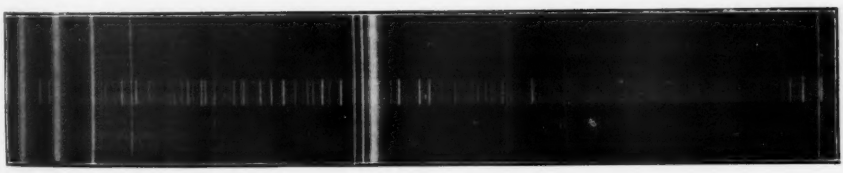
Naphthalene



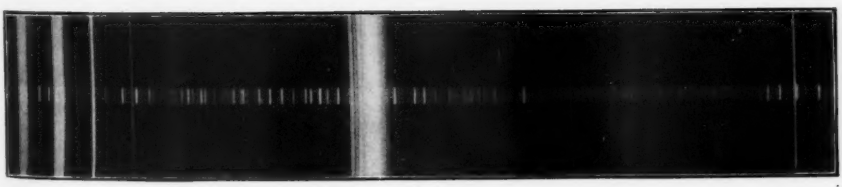
Phenyl-acetic acid
$C_6H_5 \cdot CH_2 \cdot COOH$



Oxalic acid
$(COOH)_2 \cdot 2H_2O$



Phosphorous acid
H_3PO_3



Boric acid
$B(OH)_3$

FIG. 2. Raman Spectra of Crystal Powders.

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A NEW SOLUTION OF A PROBLEM IN INVERSE PROBABILITY.

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Received January 22, 1937.

Bayes' problem has been dealt with so often that the only reason for returning to it, or rather to an amplified form of it used by K. Pearson,[1]* is that the solution of the problem now offered appears to be new and more satisfactory than those given hitherto.

Karl Pearson in the paper[1] justified the solution of Bayes' problem obtained by Bayes. This justification, however, was not considered satisfactory by F. Y. Edgeworth.[2] A different solution of Bayes' problem was given by R. A. Fisher[3] using his method of maximum likelihood.

Both these solutions do not appear to be satisfactory in that they have not taken into consideration the variations due to random sampling. Indeed Fisher himself admits, after obtaining what he calls the "*optimum*" solution, "other values of p (the solution) for which the likelihood is not much less cannot, however, be deemed unlikely values for the true value of p", *vide* page 327 of (3).

We will consider the following form of the problem which Pearson[1] has termed the "fundamental problem in practical statistics".

An "event" has occurred a times out of $a + b = c$ trials, where we have no *a priori* knowledge of the frequency of the event in the total population of occurrences. What is the probability of its occurring d times in a further $d + e = f$ trials?

We shall call the occurrence of the event a success. Our random sample of c trials in which there were a successes has been obtained from a population in which the chance of success of a random trial is some, to us unknown, value lying between 0 and 1.

In justifying Bayes' solution Pearson[1] makes two assumptions, namely, that (i) our sample was obtained from some one population out of a large number, and (ii) the chance of success of a random trial in these populations

* According to H. Levy and L. Roth, the problem of "Inverse Probability" was first considered by James Bernoulli, *vide* page 7 of their book[8]; but according to de Morgan [see page 60 of(9)] this claim should go to Bayes.

is distributed in some continuous manner from 0 to 1. Both these assumptions are open to objection. In practice there is usually only one such population.

The solution obtained by Fisher[3] suffers from the disadvantage that the chance of success in the population from which our sample was obtained may be quite different from the value obtained by the method of maximum likelihood. Indeed, the method does not tell us anything about the order of magnitude of the difference between these two values of the chance of success in the population.

We will now give a solution of the problem which is believed to be free from the objections raised above. This solution has already been indicated briefly in (4).

Let k be the chance of success of a random trial in the population from which our sample of c trials, of which a are successes, was obtained. Then the chance that in a random sample of c trials from that population there are not more than a successes is given by

$$P = l^c + {}_cC_1\, l^{c-1}\, k + \ldots\ldots + {}_cC_a\, l^b\, k^a, \quad \text{where } l = 1 - k, \text{ and } a + b = c$$
$$= I_l\,(c - a,\ a + 1) \qquad \text{(I)}$$

where $I_l\,(c - a,\ a + 1)$ is an incomplete β-function ratio written after the manner of Pearson.[5]

Although equation (I) is of the cth degree in k, it is not difficult to show that there is only one real solution between 0 and 1 (including the limits). Hence by "the solution" of equations like (I) we will mean here the unique real solution between 0 and 1 (including the limits).

Let us choose some limit for random chance, say 5%. We put $P = 0{\cdot}05$ in (I) and solve for k. The method of solution is indicated below. Let k_1 be the solution. This means that the chance of getting not more than a successes in a random sample of c trials from a population is less than $0{\cdot}05$ if the chance of success of a random trial in that population be greater than k_1; that is to say, on our limit for random chance our sample could not have been obtained from a population in which the chance of success is greater than k_1. Hence k_1 is the upper limit to k. It can be easily seen that k_1 is greater than a/c, the chance of success in the sample.

Let us now consider our sample from the point of view of failures. The chance that in a random sample of c trials there will not be more than $b\ (= c - a)$ failures is given by

$$P = k^c + {}_cC_1\, k^{c-1}\, l + \ldots\ldots + {}_cC_b\, k^a\, l^b$$
$$= I_k\,(c - b,\ b + 1) \qquad \text{(II)}$$

Putting $P = 0{\cdot}05$ we solve (II) for k. Let k_2 be the solution. Clearly k_2 is less than a/c. It can be seen in a manner similar to the above that on our limit for random chance our sample could not have been obtained from a population in which the chance of success is less than k_2. Hence k_2 is the lower limit to k. Thus

$$k_2 \leqslant k \leqslant k_1.$$

If k_1 be the chance of success in the population, the probability of obtaining d successes in a sample of f trials is

$$K_1 = \frac{f!}{d!\,e!}\, k_1^d\, l_1^e, \quad \text{where } l_1 = 1 - k_1, \text{ and } d + e = f.$$

Similarly, if k_2 be the chance of success in the population, the probability of obtaining the same sample is

$$K_2 = \frac{f!}{d!\,e!}\, k_2^d\, l_2^e, \qquad \text{where } l_2 = 1 - k_2.$$

As any value between k_2 and k_1 (including these values) is possible for the population chance, we see that the chance, K, of obtaining d successes in a sample of f trials from a population from which a previous sample of c trials had yielded a successes is given by

K lies between K_1 and K_2 (limits included) (*a*)

K_1 or $K_2 \leqslant K \leqslant K_3$, retaining the smaller of the two K_1 or K_2, (*b*),

where

$$K_3 = \frac{f!}{d!\,e!}\, k_3^d\, (1 - k_3)^e \text{ and } k_3 = \frac{d}{f}.$$

The relation (*a*) is to be used when k_3 is outside the interval k_2 to k_1, while (*b*) is to be used when $k_2 \leqslant k_3 \leqslant k_1$.

That is to say, the probability may have any value given by the appropriate relation (*a*) or (*b*), but which of these values is the true value it is impossible to say with the available data.

Before actually considering some numerical examples we will give a method of solving (I). We will assume that neither $a + 1$ nor $c - a$ is greater than 50 in which case we can make use of the tables in [5]. This assumption will be true in a large number of cases actually met with.

To solve (I) we select the table of the $I_x(p, q)$ function from [5] corresponding to $q = a + 1$, and run down the column corresponding to $p = c - a$, until we come either to a single value equal to $0{\cdot}05$ or to two consecutive values which are on either side of $0{\cdot}05$. In general we will get two values. The corresponding values of x will differ by $0{\cdot}01$. By interpolation we can

get the value of x correct to 0·001 such that the corresponding $I_x(c - a, a + 1)$ function is nearest to 0·05.†

Let x_1 be the value of x so obtained. Then $x_1 = l_1$. Hence $k_1 = 1 - x_1$.

It need hardly be mentioned that the tables (5) can be used only when $c - a \not< a + 1$, *i.e.*, when $a < \frac{1}{2} c$. If, however, $a \not< \frac{1}{2} c$ we write equation (I) as

$$1 - P = k^c + {}_cC_1 k^{c-1} l + \ldots + {}_cC_{a+1} k^{a+1} l^{c-a-1}$$
$$= I_k (a + 1, c - a) \qquad I(a)$$

and then proceed as given above. In this case the value of x obtained is the value of k itself.

In a similar manner we solve (II) and thus obtain the value of k_2.

Since the limits k_1 and k_2 were obtained on the 5% limit for random chance, we may term k_1 and k_2 as the 5% limits of the chance of success of a random trial in the population from which our sample was drawn, or briefly, k_1 and k_2 are the 5% limits from our sample, and the interval k_1 to k_2 (including the limits) the 5% interval.

Example 1. A sample of 50 bottles produced by a machine was examined and found to contain 6 defective bottles. What is the chance of producing a defective bottle by that machine?

Let the required chance be k.

To get the upper limit for k we use equation (I) which in this case, assuming 5% as our limit for random chance, becomes

$$0·05 = I_l (44, 7) \qquad (A)$$

since $44 > 7$ we can use the tables (5). On page 190 of (5) we run down the column corresponding to $p = 44$ and $q = 7$, and find that $I_{·77} = ·0397$ and $I_{·78} = ·0555$. Thus the value of x correct to two decimal places is 0·78. Interpolation gives us the value 0·777 which is l_1. Hence the upper limit $k_1 = 1 - 0·777 = 0·223$.

The lower limit for k is obtained from the equation

$$0·05 = I_k (6, 45) \qquad (B)$$

As 6 is less than 45 we transform (B) into

$$1 - 0·05 = 1 - I_k (6, 45) \text{ or}$$
$$·95 = I_l (45, 6)$$

From the appropriate column on page 167 of (5) we find that

$$I_{·94} = ·9224 \text{ and } I_{·95} = ·9622$$

† To get x more accurately is somewhat tedious, but in a large number of cases the value of x correct to two decimal places even will more than suffice.

The required value of x is $0 \cdot 947$ which is l_2.
Hence the lower limit $k_2 = 1 - 0 \cdot 947 = 0 \cdot 053$.

Thus the chance is between $0 \cdot 053$ and $0 \cdot 223$ (including the limits) of obtaining a defective bottle in the population of bottles produced by the machine from which a random sample of 50 bottles had contained 6 defective bottles.

A New Test of Significance.

The above method leads us to a new test with which to see whether two independently obtained samples are significantly different from each other. The test may be stated thus :

Choosing some limit for random chance we calculate the interval from each of the samples. The samples are to be considered significant only when the intervals do not have any common part.

Example 2. Two methods of treatment A and B were tried. A was found successful in the case of 16 persons out of 20, while only 14 out of 30 were successfully treated by B. Is A significantly better than B ?

Using 5% as our limit for random chance and proceeding as in example (1) we see that the 5% interval in the case of the treatment A is from $0 \cdot 599$ to $0 \cdot 929$ including the limits. In a like manner, the 5% interval in the case B is found to be $0 \cdot 308$ to $0 \cdot 630$ including these limits.

Comparing the intervals we see that they have a common part. Hence the two treatments are not significantly different from each other on our 5% limit for random chance.

It may be mentioned, in passing, that if we are content to obtain the solutions correct to two figures only—and this is quite sufficient for many purposes—the whole test can be worked out in less than two minutes with the help of tables ([5]).

The test can be further simplified thus : If the lower limit for that sample, in which the chance of success is greater, be above the upper limit for the other sample, then the two samples can be considered to be significantly different from each other.

This means that only two limits, instead of four, need be worked out.

In the above example, the chance of success in sample A is 16/20 or $\cdot 8$ and that in B is 14/30 or $\cdot 47$. We thus need calculate only the lower limit for the chance of success in the A population and the upper limit in the case of B. The former is $0 \cdot 59$ and is not above the latter which is $0 \cdot 630$. Hence

the two samples are not significantly different from each other on our 5% level of random chance.

This simplification reduces the time required for the application of the test.

In addition to the quickness of application of this test another great merit this test possesses is that *no assumption has been made except that the population corresponding to each sample is one and one only.* A little reflection will tell us that this assumption holds in all cases of practical interest.

This test may be compared with that given by E. C. Rhodes[6] in which he assumes that the most probable value of the chance of success in the population is the geometric mean between the chances of success in the two samples. In a note to that paper K. Pearson[7] deduces Rhodes' result without making his specific assumption, but on another assumption, namely, that the chance of success in the population from which the samples were obtained is some value between the two chances in the two samples. One objection to this test is that variation due to random sampling has not been taken into account. It is intended to discuss Rhods' test separately in a subsequent paper.

It is now suggested that the problem as stated by K. Pearson[1] requires a slight modification as may be seen from the following. Consider the case in which a treatment was found to be successful in the case of say 16 people out of 20. If the same treatment is to be used in the case of the next 30 people, what we would like to know is not so much the chance that say, 18 people will be treated successfully, as the chance that *at least* 18 people will be treated successfully. Hence it appears necessary that the wording of the problem as given by Pearson[1] will have to be slightly amended to the following :—

An " event " has occurred a times out of $a + b = c$ trials, where we have no *a priori* knowledge of the frequency of the event in the total population of occurrences. What is the probability of its occurring at least d times in a further $d + e = f$ trials ?

We may proceed to solve this as follows.

Our sample of c trials contains a successes. As explained above we find the two limits on some assumed limit for random chance. Let k_1 and k_2 $(k_1 > k_2)$ be the two limits.

If k_1 be the chance of success in the population, the chance of obtaining at least d successes in f trials is given by

$$K_1' = I_{k_1}\ (d,\ f + 1 - d) \qquad \text{(III)}$$

K_1' can be found from the tables[(5)].

Similarly assuming k_2 to be the chance of success in the population, the chance of obtaining at least d successes in f trials is

$$K_2' = I_{k_2}(d, f + 1 - d) \qquad \text{(IV)}$$

K_2' can be evaluated.

Since k, the populution chance, is some value given by $k_2 \leqslant k \leqslant k_1$, we see that when a random sample of c trials from a population was found to contain a successes, the chance, K', that a subsequent sample of f trials from the same population will contain at least d successes is given by

$$K_2' \leqslant K' \leqslant K_1'$$

Example 3. 16 people out of 20 were successfully treated with a certain medicine. What is the chance that the medicine will be found successful in the case of at least 18 people out of the next 30 people on whom it is tried?

Using 5% as our limit for random chance, we find that the two limits, k_2 and k_1, are

0·599 and 0·929.....See example (1).

From equation (IV)

$$K_1' = I_{.929}(18, 13)$$
$$= 1{\cdot}000.....\text{using the tables } (^5).$$

Similarly $K_2' = I_{.599}(18, 13) = {\cdot}574.$

Thus when 16 people out of 20 were successfully treated, the chance that the same treatment will be found successful in at least 18 out of the next 30 people is some value between ·574 and 1·000, including these values.

Replication of an Experiment.

We will now show how a further repetition of an experiment enables us to improve upon the information already obtained.

Thus let us suppose that a first sample of c trials yielded a successes and a next sample of f from the same infinite population gave d successes. What are the limits of the chance of success of a random trial in the population from which these two samples were drawn?

Let k be the chance of success in the population. Then the chance that in a sample of c trials there are not more than a successes is

$$p_1 = I_l(c - a, a + 1)$$

Similarly the chance that in a sample of f there should not be more than d successes is

$$p_2 = I_l(f - d, d + 1).$$

Hence the combined chance of obtaining not more than a successes in

one random sample of c trials and not more than d successes in the other sample of f trials is given by

$$P = p_1 . \quad p_2 = I_l\ (c - a,\ a + 1) . \quad I_l\ (f - d,\ d + 1) \qquad \text{(i)}$$

Taking the failures into consideration for the lower limit we see in a similar manner that the combined chance is

$$P = I_k\ (a,\ c - a + 1) . \quad I_k\ (d,\ f - d + 1) \qquad \text{(ii)}$$

Putting $P = 0{\cdot}05$, corresponding to our 5% limit for random chance, we solve (i) for k. (The method of solution is slightly tedious and is explained below.) This value of k is the upper limit for the chance of success.

Similarly putting $P = 0{\cdot}05$ in (ii) and solving for k we get the lower limit to the chance of success.

Suppose k_1 is the upper limit. Then k_1 is the solution of (i). Hence

$$p_1 = I_{1-k_1}\ (c - a,\ a + 1) \qquad \text{(iii)}$$

Since p_1 and p_2 are both positive fractions we see that p_1 and p_2 are each greater than P, as $P = p_1\, p_2$.

If we had knowledge of one sample only, say that out of c trials a had been successes, the equation for the upper limit for the population chance would have been

$$P = I_{1-k_3}\ (c - a,\ a + 1) \qquad \text{(iv)}$$

Comparing (iii) and (iv) we can easily see that

$$k_1 < k_3 \text{ since } p_1 > P.$$

That is to say, we get a lower value for the upper limit of the population chance of success when we have knowledge of two samples from that population than from one.

Similarly we can see that the second sample increases the lower limit of the population chance. Thus the interval between the two limits gets diminished from both ends.

We can generalise this further and say that each extra sample contracts this interval, but that there is a limit to this contraction will be clear later on.

To solve (i) for k after putting $P = 0{\cdot}05$ we proceed as follows.

Suppose $c > 2\,a$ and $f > 2\,d$. From the tables ([5]) we use the column corresponding to $p = c - a$ for $q = a + 1$ and the column corresponding to $p = f - d$ and $q = d + 1$. We find a value of x such that the product of the corresponding functions in those columns is either $0{\cdot}05$ or as near it as possible. In general we find two values of x differing by $0{\cdot}01$ such that the corresponding products are on either side of $0{\cdot}05$, and then, if necessary, we can find by interpolation the value of x correct to the third decimal place.

Let x_1 be the value. The upper limit to the chance of success in the population is then given by $k_1 = 1 - x_1$.

While solving (ii) we note that, since $a < \frac{1}{2}c$ and $d < \frac{1}{2}f$, we have to rewrite (ii) as

$$0{\cdot}05 = [1 - I_l(c - a + 1, a)]\,[1 - I_l(f - d + 1, d)] \qquad \text{(v)}$$

These I_l's can now be found from the tables ([5]). As explained above we will find in general two values of x differing by ·01 such that the products on the *r.h.* of (v) are on either side of 0·05, and then, if necessary, we may find by interpolation the value of x correct to 3 decimal places. If x_2 be this value then $k_2 = 1 - x_2$.

If only either $a < \frac{1}{2}c$ or $d < \frac{1}{2}f$, a method of solving (i) and (ii) using the tables ([5]) can be easily devised. The method, however, is slightly more tedious.

Example 4. A sample of 50 bottles was found to contain 6 defective bottles, while another sample of 30 had 7 defective bottles. What is the population chance of finding a defective bottle ?

Using 5% as our limit for random chance equation (i) becomes

$$0{\cdot}05 = I_l\,(44, 7).\quad I_l\,(23, 8).$$

Using tables ([5]) we find that for

$x = 0{\cdot}78$ the product is ·0370 and for
$x = 0{\cdot}79$ the product is ·0546.

Thus the nearest value is $x = 0{\cdot}79$.

Hence the upper limit is $1 - 0{\cdot}79 = 0{\cdot}21$.

For the lower limit we use equation (v) which, in this case, becomes

$$0{\cdot}05 = [1 - I_l\,(45, 6)]\,[1 - I_l\,(24, 7)]$$

Using tables ([5]) we see that

for $x = 0{\cdot}87$ the product is ·0556 and
for $x = 0{\cdot}88$ the product is ·0345.

The nearest value is $x = 0{\cdot}87$. Thus the lower limit is

$$k_2 = 1 - 0{\cdot}87 = 0{\cdot}13.$$

Hence the 5% interval is 0·13 to 0·21.

When we had knowledge of only the first sample the corresponding 5% interval was

0·053 to 0·223..... [See example (1).]

The second sample has thus enabled us to reduce the 5% interval.

We can extend the above method to the case where we have more than two samples. The tediousness of the calculations, clearly, increases with

the number of samples. The calculations are, however, very much simplified when successive equal random samples have yielded identical results. Although this example is mainly of theoretical interest, nevertheless it serves to give us an idea as to how the calculated limits for the success of a random trial in the population vary with the increasing number of samples.

Suppose we take n random samples of c trials each and find that there are a successes in each sample. What are the limits for the population chance of success of a random trial ?

Let k be the population chance of success. The chance of obtaining not more than a successes in a random sample of c trials is given by

$$p = \mathrm{I}_l\ (c - a,\ a + 1)$$

Hence the combined chance of obtaining n such samples is

$$\mathrm{P} = p^n = [\mathrm{I}_l\ (c - a,\ a + 1)]^n.$$

$$\therefore\ \ \mathrm{I}_l\ (c - a,\ a + 1) = \mathrm{P}^{\frac{1}{n}} \qquad \text{(vi)}$$

If we put $\mathrm{P} = 0{\cdot}05$, corresponding to the 5% limit for random chance and slove (vi) for k we get the higher limit to the population chance of success.

Let us denote this upper limit by ${}_nk_1$.

As $n \to \infty$, $\mathrm{P}^{\frac{1}{n}} \to 1$. Hence ${}_nk_1 \to 0$ as may be seen from (vi) or otherwise.

That is to say, the upper limit tends to zero as n tends to infinity.

Similarly we can see that the lower limit, ${}_nk_2$, tends to 1 as n tends to infinity.

Thus as n increases from 1 onwards, ${}_nk_1$ and ${}_nk_2$ approach each other, *i.e.*, the interval between the limits decreases with the increase in n. There is, however, some value n_1 depending upon the value of P such that

$${}_{n_1}k_2 \leqslant {}_{n_1}k_1, \text{ but } {}_{n_1+1}k_2 > {}_{n_1+1}k_1.$$

This shows that for $n > n_1$, the lower limit exceeds the upper limit, an apparently absurd result. This result, however, means the following.

We cannot obtain by random chance more than n_1 equal successive samples giving identical results, where n_1 depends upon the result in a sample and the limit for random chance assumed by us. But if we do get more than n_1 such samples, we may conclude that the individuals in the sample had not been obtained from the same population. This will be clearer from the following example.

Suppose we throw twelve dice. A single throw is a random sample containing 12 trials. If we assume that all the dice are identical in all respects so long as there is nothing against this supposition, we can consider

that each trial is from the same population, although the 12 trials in a sample throw are obtained from 12 different dice. Let us say that a throw of more than 3 from a dice is to be considered a success.

Suppose the first throw contains 4 successes and 8 failures.

The following table gives the two limits on the 5% limit for random chance.

TABLE.

No. of throws m	Limit for the population chance of success	
	Lower	Upper
1	0·12	0·61
2	0·21	0·49
3	0·26	0·43
4	0·29	0·39
5	0·31	0·36
6	0·33	0·34
7	0·35	0·33

The limits for further values of m are not calculated as the lower limit for $m = 7$ exceeds the upper limit.

Suppose we are told that the dice are flat pieces so that there are only two faces for each die which can turn up. Before the first throw is made there are three possible values for the population chance of success, namely, 0, 0·5 and 1. After seeing the first throw which gave 8 failures and 4 successes, the population chance of success can clearly be only 0·5. Since this chance is between the two limits for $m = 1$, we see that our sample could have been obtained by random chance, the limit for which being 5%. When the second throw gave us the same result, we see that our population chance, namely 0·5, is outside the limits for $m = 2$. Hence we conclude that our assumption that the dice were identically marked is not correct.

On the other hand, suppose that the dice used are true and cubical in shape. In this case the possible values for the population chance are 0, $\frac{1}{6}$, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, $\frac{5}{6}$ and 1. After the first throw, the possible values for the chance of success dwindle to $\frac{1}{6}$, $\frac{1}{3}$ and $\frac{1}{2}$. The second throw restricts the value to $\frac{1}{3}$. After the seventh throw we conclude that the dice are not identically marked.

It is also clear that if the 12 dice are identical in all respects, then whatever may be their shape and howsoever they may be marked, it will

not be possible to obtain by random chance, the limit for which is 5%, more than 6 successive throws in each of which we obtain 4 successes and 8 failures. It is intended to discuss this problem in more detail in the near future.

Conclusion.

We have given in the foregoing a new method for solving a problem which is generally referred to under " inverse probability ". It is clear that our method takes into account the variation due to random sampling and hence our solution is essentially a " statistical " solution. It also appears to be free from the objections that have been raised so far against the solutions of the problem that have been offered hitherto and hence it may be considered to be the most satisfactory of all the solutions given so far.

The theory of inverse or inductive probability, which was given a place in the theory of probability by de Morgan and la Place, was thrown out especially by Boole, Venn and Chrystal. An attempt to reinstate it was made by Karl Pearson, see for example ([1]), and is still being made notably by H. Jeffreys among others, as may be seen from many papers published by him of which, ([10]) to mention only one, may be consulted. The chief opponent to this view appears to be R. A. Fisher who says on page 10 of ([11]) that it is " my personal conviction, which I have sustained elsewhere, that the theory of inverse probability is founded upon an error, and must be wholly rejected ". Similar views will be found expressed on pages 6-8 of his later book ([9]). The following sentence expresses his opinion very crisply and forcibly. On page 8 of ([9]) we read " whatever the reasons are which give experimenters confidence that they can draw valid conclusions from their results, they seem to act just as powerfully whether the experimenter has heard of the theory of inverse probability or not ".

I venture to submit that the reason for these divergent views lies in the fact that the supporters of the theory of inverse probability have been claiming for it much more than it can really indicate, with the result that the opponents have very rightly contested the claim and, as far as I can judge, their criticisms have not been satisfactorily answered by the exponents of the theory.

It is believed that the method of solution given in this paper shows a way out of this *impasse*, and that it will enable the theory of inverse probability to be given its rightful place in the mathematical theory of probability.

This method is being applied to other problems depending upon inductive probability. The results will be published in due course.

Summary.

A new solution, which may be termed a "statistical" solution, has been given in this paper of a problem in inverse probability called "The fundamental problem in practical statistics" by K. Pearson.[1] This solution takes into account the variation due to random sampling and is hence believed to be the most satisfactory solution of the problem offered so far. It is also believed that it will be possible now for the theory of inverse probability to be given its rightful place in the mathematical theory of probability.

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SOME REMARKS ON THE BIRGE-SPONER METHOD OF VIBRATIONAL EXTRAPOLATION.

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The correlation of molecular and atomic terms is of great importance for the determination of the electronic configuration of the diatomic molecule and therefore for any conclusion, derived therefrom. For such correlation, a knowledge of the excitation energy E of the dissociation products is essential. In most cases this is obtained by a linear extrapolation of the vibrational levels, which gives the dissociation energy D″ of the ground state and D′ of the excited level. This procedure, as is well-known, more often than not, gives for the dissociation energy an absolute value, which is too high. The energy of excitation of the dissociation products, however, is related to the D values by the formula :

$$E = \nu_0 + D' - D'' ;$$

ν_0 being the energy of the origin of the band system. We intend to show that in many cases E is therefore determined to a higher degree of accuracy than either D″ or D′ because it does not depend on their absolute values but on their difference only. In the present paper we shall compare the values of E obtained by such extrapolation with those derived from direct experimental observation. These examples comprise also ionised molecules for which the above formula reads :

$$J_A = J_M + D''(M^+) - D''(M),$$

where J_A is the ionisation potential of the constituent atom, J_M that of the molecule, and D″ (M^+) and D″ (M) are the dissociation energies of the ground levels of the molecule in the ionised and the neutral states respectively.

As a first example we take the molecules N_2 and N_2^+. The energy of dissociation (D″) of N_2 in its ground state $X\,^1\Sigma$ is known from various considerations and particularly from predissociation data to be 7·35 e-volts. The ionisation potential (J) of the N_2 molecule[1] and of the N atom,[2] namely 15·65 and 14·48 e.v. respectively, being experimentally known D″ (N_2^+) can be calculated as follows :—

$$D''(N_2^+) = D''(N_2) + J(N) - J(N_2) = 6{\cdot}18 \text{ e.v.}$$

From extrapolation of the vibrational levels, we get D″ (N_2 $X^1\Sigma$) = 11·75 e.v. This value is obtained from the constants[1] $\omega''_e = 2359{\cdot}60$ and $\omega''_e x''_e = 14{,}445$. The great discrepancy between the actual value of 7·35 and the extrapolated one of 11·75 e.v. is not due to inaccuracy in ω'' because this is directly confirmed by the Raman spectrum. The anharmonic constant, however, is by no means accurate, in spite of the wealth of experimental details from which it is deduced. If we arrange the observed bands of the Lyman–Birge–Hopfield system[3] into the usual Deslandres scheme, we obtain the following second differences :—

$$2\ \omega''x'' = 39{\cdot}4 \quad 22{\cdot}5 \quad 37{\cdot}1 \quad 16{\cdot}0 \quad 37{\cdot}1 \quad \ldots.$$

These are the means obtained from the seven v' progressions, in which nearly each vibrational level $v'' = 0$ to $v'' = 6$ is fixed by at least 4, but more often by 6 to 7 independent measurements. The deviation of these experimental values from the accepted values deduced for the whole system $2\ \omega''x'' = 28{\cdot}89$ is no doubt due in some measure to the facts, that the measurements concern heads and not origins and that the bands lie in the Schumann region where on account of the obvious experimental difficulties relatively larger inaccuracies are to be expected, the more so since here a small error in λ brings about a large one in ν.

In a similar way the extrapolation of D″ (N_2^+) by means of the constants[1] $\omega''_e = 2206{\cdot}84$, $\omega''_e x''_e = 16{\cdot}044$ yields the value 9·23 e.v. In this case using the data of Merton and Pilley[4] we obtain the following second differences as the mean values from the first seven v' progressions which again are the experimentally best known :—

$$2\ \omega''x'' = 32{\cdot}4 \quad 33{\cdot}3 \quad 32{\cdot}8 \quad 29{\cdot}9 \quad 34{\cdot}6.$$

The divergence from the accepted value 32·09 is much less than in the above case, the bands lying in the visible and near ultra-violet spectrum. It is worthy of note that the discrepancy between the actual value of D″ = 6·18 and the extrapolated one of 9·23 is nearly as big as in the case of N_2. Extrapolating D″ (N_2^+) with three constants given by Watson and Koontz[4] we get 8·06 e.v., but for the sake of consistency J(N) is calculated by means of the value obtained by two constants only as in N_2.

Using these extrapolated values for the energy of dissociation and replacing in the formula $E = \nu_0 + D' - D''$, ν_0 by J (N_2) and D′ by D″ (N_2^+) we can now calculate J (N).

$$\begin{aligned} J\,(N) &= J\,(N_2) + D''\,(N_2^+) - D''\,(N_2) \\ &= 15{\cdot}65 + 9{\cdot}23 - 11{\cdot}75 \\ &= 13{\cdot}13 \text{ e.v.} \end{aligned}$$

This value is very close to the actual value 14·48. Considering the term system of N_2^+ as an extension of that of N_2 and J (N) as an energy of excitation of dissociation products we can say that its value derived from vibrational extrapolation is only incorrect by less than 10 per cent. whereas D″ [= D″ (N_2)] is incorrect by about 60 per cent. and D′ [= D″ (N_2^+)] by about 50 per cent.

Similar results are obtained for CO and CO^+. We have shown elsewhere[5] that D″ (CO) lies between 10·5 and 9·6 e.v. and we use here the value 10·45 e.v.[6] The ionisation potential of the CO molecule and of the constituent atoms are well known.[1,2] It is generally assumed that the ground level of CO^+ is formed by combination of C^+ (^2P) + O (^3P). In this case D″ (CO^+) can be calculated as follows :—

$$\begin{aligned} D''(CO^+) &= D''(CO) + J(C) - J(CO) \\ &= 10{\cdot}45 + 11{\cdot}22 - 14{\cdot}1 = 7{\cdot}57 \text{ e.v.} \end{aligned}$$

If, however, CO^+ ($X^2\Sigma$) arises from C (^3P) + O^+ (^4S), the value J (O) = 13·55 e.v. yields 9·9 e.v. for D″ (CO^+).

The vibrational extrapolation for D″ (CO^+) using[1] $\omega''_e = 2211{\cdot}1$ and $\omega''_e x''_e = 15{\cdot}12$ gives 9·84 e.v. Similarly the level $X\,^1\Sigma$ of CO gives on extrapolation D″ (CO) = 10·95 e.v. with the constants[7] $\omega''_e = 2168{\cdot}7$ and $\omega''_e x''_e = 13{\cdot}1$.* This is another case where we should expect the inaccuracy of extrapolation to be brought about by the uncertainty of the magnitude of the anharmonic constant, for ω''_e is fixed by the agreement between the results from band spectra and Raman effect.

These considerations lead us to the following cycle :—

$$\begin{aligned} J(O) \text{ or } J(C) &= J(CO) + D''(CO^+) - D''(CO) \\ &= 14{\cdot}1 + 9{\cdot}8 - 10{\cdot}95 = 13{\cdot}0 \text{ e.v.} \end{aligned}$$

This value compares favourably as well with J (C) = 11·22 as with J(O) = 13·55. To our mind the latter interpretation is the nearer to reality because combination of $C^+ + O$ admits the possibility of only one bond in the pair-bond theory and the dissociation energy of such a molecule should be of the order of 5 e.v. On the other hand, the combination of $C + O^+$ gives a double bond, both the p-electrons of C remaining intact and D″ (CO^+) will be of the order of 10 e.v. The extrapolated value agrees with this conclusion. Furthermore, in this case the term $A^2\Pi$ would be the lowest of the combination $C^+ + O$ and its extrapolated energy of dissociation, 5·27 e.v., is of the right order of magnitude for a single link. The intersection

* The value 13·1 for ωx corresponds to Read's value 13.28 when the third power is neglected.

of the potential curves would then be real and the energy difference of the dissociation products which amounts to about 2 e.v. again agrees with

$$J(O) - J(C) = 2{\cdot}3 \text{ e.v.}$$

As a third example we consider the molecules O_2 and O_2^+. Using the values[8] $D''(O_2) = 5{\cdot}05$, obtained from direct observation of the convergence point, and the accepted values[1,2] $J(O_2) = 12{\cdot}5$ and $J(O) = 13{\cdot}55$ e.v., we obtain for $D''(O_2^+)$ 6·10 e.v.

For $D''(O_2)$ Birge and Sponer extrapolated the value 6·65 e.v. and Herzberg[9] obtains 5·67 e.v. by means of a formula involving higher powers of v''. For O_2^+ using[1] $\omega''_e = 1876{\cdot}4$ and $\omega''_e x''_e = 16{\cdot}53$ we obtain 6·45 e.v. for $D''(X\,^2\Pi)$. Employing the same cycle with these extrapolated values we obtain $J(O) = 12{\cdot}30$ [with $D''(O_2) = 6{\cdot}65$] and 13·28 [with $D''(O_2) = 5{\cdot}67$]. It will be seen, that here again the agreement between the calculated and the real J (O) is better than that between the extrapolated and the actual energies of dissociation of the two ground states. The discrepancy between the actual and the extrapolated value is about 6 per cent. for $D''(O_2^+)$ and about 30 or 12 per cent. for $D''(O_2)$, whereas for J (O) the discrepancy is about 9 or 2 per cent. according to the value employed for $D''(O_2)$.

The energy of dissociation of the ground level $X\,^2\Pi$ of the molecule NO formed by unexcited atoms can be calculated from its heat of formation[3] (− 21·6 K cal./mol.) by means of Born's cycle and is 5·3 e.v. The products of dissociation of the excited term $A\,^2\Sigma$ are unexcited O and N in the term ($2s^2\,2p^2\,3s$, ^{4}P), 10·29 e.v. above the ground term. There is little doubt about the correctness of this correlation, since it has been confirmed by the band spectra of PO, AsO and SbO. NO, therefore, is one of the few molecules for which the energy of dissociation both for the ground state and for the excited state are known to a high degree of accuracy quite independently of the extrapolation method. Thus we obtain,

$$\begin{aligned} D'(A\,^2\Sigma) &= \nu_0 + E - D''(^2\Pi) \\ &= 5{\cdot}46 + 10{\cdot}29 - 5{\cdot}3 = 10{\cdot}5 \text{ e.v.} \end{aligned}$$

From the extrapolation of the vibrational levels, $D''(X\,^2\Pi)$ and $D'(A\,^2\Sigma$- have been calculated earlier[10] as 6·70 and 10·67 e.v. respectively. Introducing these extrapolated values in the above cycle, we obtain E ($N\,^4$P) = 9·43 e.v. which is less than 10 per cent. incorrect whereas the extrapolated values of D′ and D″ are out by 2 and 28 per cent. respectively.

The molecule Na_2 is another example where although the extrapolated values for the energies of dissociation D″ and D′ are unusually too high, the excitation energy of the dissociation products is given correctly. The green

band system $C\ ^1\Pi_u \leftrightarrows A\ ^1\Sigma_g$ of this molecule exhibits the v' levels almost to the point of convergence and since the correlation of the atomic levels to the molecular ones is certain, D′ and D″ have been calculated by the above cycle as 0·35 and 0·76 e.v. respectively.[1] Extrapolation using the accepted constants yields 0·74 and 1·07 e.v. respectively. We obtain from these latter data E ($^2P - {}^2S$) of Na = 2·18 e.v. while the actual value is 2·09 e.v.[2] It will be seen that the error is less than 5 per cent. even though the individual errors in absolute values of D′ and D″ are 110 and 40 per cent. respectively.

These examples make it clear that under certain conditions it is possible to use the extrapolated values of dissociation for purposes of correlation between atomic and molecular levels. For, such a procedure does not necessarily involve an accurate knowledge of the absolute values of D″ and D′ but only their difference D′ − D″, and in forming this difference the errors in D′ and D″, more or less cancel out in many cases. A correct description of the complete vibrational function of a molecule cannot be expected to be given by neglecting powers of v higher than 2. The deviation of the actual law of force prevailing in a molecule from that of the simple harmonic oscillator is greater than what can be accounted for by the second power only. In certain cases such a formula is found insufficient to fit even a small number of low vibrational levels. Hence the extrapolation of the linear formula always leads to too high values as well of D′ as D″. The errors therefore almost always run in the same direction. In a case in which both D′ and D″ are extrapolated with vibrational functions of the same accuracy, the excitation energy E should be the more correct the more D′ and D″ are roughly of the same order of magnitude. Such a condition is fulfilled in most of the known band spectra for which correlations have been proposed. That the errors cancel out almost completely as *e.g.* in Na_2 is of course more or less fortuitous.

On the other hand, it is remarkable that a high accuracy in one of the dissociation energies coupled with the normal error of extrapolation in the other one always leads to entirely incorrect results in E. We take for instance the I_2 molecule. In this case, from the well-determined convergence point and the known energy of excitation of the iodine atom, the following energies of dissociation have been derived: D″ ($X\ ^1\Sigma_g$) = 1·53, D′ ($A\ 1_u$) = 0·08, D′ ($B\ O_u$) = 0·55 e.v. The linear extrapolation with the accepted constants gives for these 2·38, 0·06 and 0·60 e.v. respectively. Of these, the two excited levels A and B have vibrational levels which are traced almost to the limit of convergence and therefore the vibrational

functions are more accurately known, whereas only a few low levels are observed for the ground level whose vibrational function therefore is only roughly represented. The cycle $E = \nu_0 + D'(B) - D''(X) = 1{\cdot}93 + 0{\cdot}60 - 2{\cdot}38 = 0{\cdot}15$ therefore, gives only about 16 per cent. of the actual value 0·94, because the error of extrapolation of D″(X) is not counterbalanced by that of D′(B). If however D″(X) in this cycle is replaced by ν_0 (A) *plus* the extrapolated value of D′(A) which level is known from the infra-red bands to a similar degree of accuracy as (B) O_u, we obtain $E = 1{\cdot}93 + 0{\cdot}60 - (1{\cdot}45 + 0{\cdot}06) = 1{\cdot}02$ which is only 10 per cent. higher than the actual value. Similar circumstances occur in the other halogens and in O_2, where on account of the observed convergence point in absorption, a large number of vibrational levels of the upper term are known while the ground state is known only with a few vibrational levels.

It has been recognised early that the accuracy of the dissociation energy is the greater, the shorter the extrapolation, *i.e.*, the greater the number of vibrational levels observed. Of the two constants on which D depends, ω is known experimentally with a fair degree of accuracy and its values can be checked in various ways. The true position of the origin of the band system and therefore the correct numbering of the vibrational levels can be accurately fixed by the isotope effect and by the origin of intercombination systems, wherever available. Approximate check is moreover provided by the intensity distribution and by a number of empirical rules. Inaccuracies in D mainly arise therefore from inaccuracy in ωx whose accurate determination as a second difference needs a larger number of observations. From this it follows that for a really accurate value of D we need to observe not only a large number of vibrational levels but that these levels should not show pronounced perturbations. Furthermore the accuracy of the spacing of these levels should be ensured by as many independent observations as possible. For instance, only two very long sequences enable us to observe a large number of vibrational levels but each of them only once. Such cases are by no means uncommon, *e.g.*, we get them in molecules of the type CaF. The correlation of the atomic and molecular levels in these molecules is so uniform that E in these cases is satisfactorily deduced from the linear extrapolation, evidently because the errors in the absolute values of the energies of dissociation in any one molecule are expected, as we have said above, to be in the same sense and of the same order of magnitude. The actual D values, however, are probably incorrect.

In order to bring about such a uniformity in error of D values it is obviously necessary that the terms in question should be comparable not only

as regards the number of vibrational levels but also with respect to the number of independent observations of each of them. If this condition does not obtain we sometimes come accross very strange results. An example is afforded by SiCl. The band spectrum of this molecule has been measured several times, recently finally by Jevons.[11] Extrapolation for the ground level X and the excited level B gives $D'' = 4 \cdot 0$ and $D' = 10 \cdot 8$ e.v. The excited level B being $4 \cdot 22$ e.v. above X the excitation energy E of its dissociation products is $11 \cdot 0$ e.v. which is higher than the ionisation potential of Si, *viz.*, $8 \cdot 12$ e.v. From comparison with the corresponding B level of SiF it can be seen[12] that the dissociation products will be unexcited Cl and Si in the term $3s^2 3p 4p\,{}^1S$, with an energy of excitation of $6 \cdot 16$ e.v.[2] To our mind, this glaring discrepancy is undoubtedly due to the fact that the levels $v'' = 0$ to $v'' = 5$ of the ground level X are known from 4 to 8 independent observations, whereas though the levels $v' = 0$ and $v' = 1$ are known with a similar accuracy as the corresponding v'' levels, $v' = 2$ and 3 are represented by only one band each. Since ω' is calculated by the first difference of the observed frequencies and $\omega' x'$ by the second difference, these observations are sufficient for a fairly accurate determination of ω' but yield a value of $\omega' x'$ which is too low.

We have restricted ourselves in this paper to those spectra and electronic levels of molecules for which the vibrational analysis is obviously essentially correct. It is clear that if such an analysis is itself open to objection, conclusions derived therefrom will have little meaning. We take as an example the molecule CaO. The spectrum of this molecule gives rise to bands in three regions, namely, the near infra-red, blue and the near ultraviolet.[1] These three groups of bands when analysed into three systems showed no relation among themselves and had no electronic term in common. A definite correlation is therefore not possible until the relative positions of these six terms are definitely fixed. Mahanti,[13] however, has proposed certain correlations with a view to explain the structure of the molecule analogous to that of BeO and MgO. Recently Brodersen[14] proposes a different structure on the basis of an analysis which splits these three systems into ten, most of them being of a fragmentary character. In a large number of given bands where on account of perturbations it is not always possible to give an analysis free from wide discrepancies in $\Delta G(v)$ values, it happens that a few bands which show more uniform differences can be picked out and the band systems split up into a number of independent systems. In view of our knowledge of such discrepancies in almost all extensive band systems, such a procedure is open to serious objection. Moreover, Brodersen's analysis does not avoid such discrepancies at all. For example, his systems

VI and VII should have the same final state as Mahanti's ultra-violet system. The latter system gives the following values of $\Delta G(v'')$ for the progressions $v' = 0$ and 1:—

$\Delta G(v'')$ *values.*

$v' = 0$	718·4	710·3	703·7	697·3	689·9	
$2\omega x$		8·1	6·6	6·4	7·4	
$v' = 1$	718·3	710·4	703·8	696·9	690·7	682·8
$2\omega x$		7·9	6·6	6·9	6·2	7·9

The corresponding values for the band systems VI and VII of Brodersen are given below :—

System VI	$v' = 0$	718	711	704	695
	$2\omega x$		7	7	9
	$v' = 1$		711	704	695
	$2\omega x$			7	9
System VII	$v' = 0$	721	711	704	697
	$2\omega x$		10	7	11
	$v' = 1$	724	715	699	
	$2\omega x$		9	16	

The mean values for ω and $2\ \omega x$ obtained by Mahanti[15] for all the observed ultra-violet bands are 718·3 and 7·12 respectively. The mean for $2\omega x$ derived from the values obtained from systems VI and VII together is 9·2. If we grant that the three levels are identical, it is obvious that no accurate value of ωx can be deduced for this level and therefore of the energy of dissociation. This alone is sufficient to show that correlation of molecular and atomic terms is not possible for this molecule at the present moment. Moreover, the relative positions of the electronic levels of the molecule are

by no means conclusively established. The conditions necessary for correlation discussed above are not fulfilled and this case cannot be compared to the previous ones described in this paper.

A correlation of molecular to atomic levels appears therefore possible, by the method of vibrational extrapolation, if the probable error in D″ and D′ is in the same sense (equal, positive or negative curvature, for both $\omega : v$ curves), if D″ and D′ are of comparable order of magnitude, and are known from observations of about equal accuracy. Under these conditions, it is always possible to have correct correlation, provided those atomic terms of the products of dissociation which by their L and S nature are at all possible, are not too numerous in the region in question.

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NOTE ON THE STRUCTURE OF N_2^+ AND ITS BEARING ON THE THEORY OF VALENCY.

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Recently we have discussed relations between bond energies and electronic configurations in a number of diatomic molecules.[1] In the present paper we intend to apply the same ideas to the molecule (N_2^+) for which the actual value of D″ ($X\ ^2\Sigma$) has been calculated in the preceding communication.[2]

The molecule N_2^+ has the same number of electrons as CN and is therefore of special interest. It may be recalled that Heitler and Herzberg[3] tried to interpret the dissociation products of the ground level of CN as C $sp^3\ ^5S + N\ ^4S$, but this correlation was untenable because the excitation energy of C ^5S is much larger than these authors supposed. Now-a-days it is generally assumed that the intersections of the potential curves indicated by the vibrational extrapolation are not real. The C $^2\Sigma$ term of N_2^+ recently found by Watson and Koontz[4] 6·67 e.v., above ($X\ ^2\Sigma$) shows however, an energy of dissociation which is much bigger than that of the ground level. Vibrational extrapolation neglecting the cubic term with $\omega_e y_e$, gives for D ($X\ ^2\Sigma$), 9·23, for D ($B\ ^2\Sigma$), 8·46 using the accepted constants and D ($C\ ^2\Sigma$), 13·84 e.v. with constants given by Watson and Koontz. The excitation energies of the dissociation products are therefcre 2·58 e.v. for $B\ ^2\Sigma$ and 11·28 for $C\ ^2\Sigma$ (see Fig. 1).* (B) $^2\Sigma$ lies 3·15 e.v. above the ground level of the molecule.

The electronic configuration of the ground level of N_2^+ is[5] :—

$$2s\sigma^2\ (2s) \qquad 3p\sigma^2\ (2s) \qquad 2p\pi^4\ (2p) \qquad 3s\sigma\ (2p) \qquad X\ ^2\Sigma.$$

This is the energetically lowest possible configuration for the internuclear distance prevailing in N_2^+. The excitation of the single $3s\sigma$ $(2p)$ electron to the following π^* group produces a $^2\Pi$ term as actually observed in CN but not yet in N_2^+. The groups next in order, are σ^* $(2p)$ and σ $(3s)$. Therefore the term $B\ ^2\Sigma$ has the configuration,

$$\ldots\ \ldots \qquad 2p\pi^4\ (2p)\ \ldots\ \ldots\ 4p\sigma\ (2p) \qquad B^2\Sigma$$

and similarly the term $C\ ^2\Sigma$ has,

$$\ldots\ \ldots \qquad 2p\pi^4\ (2p)\ \ldots\ \ldots\ 3d\sigma\ (3s) \qquad C^2\Sigma$$

* The extrapolation taking into account the cubic terms in the equation given by Watson and Koontz yields D ($X\ ^2\Sigma$) = 8·06 and D ($C\ ^2\Sigma$) = 11·59 e. v. The excitation energy will then be E = 10·20 e. v., which is almost exactly the value of N ^4P at 10·29 e.v.

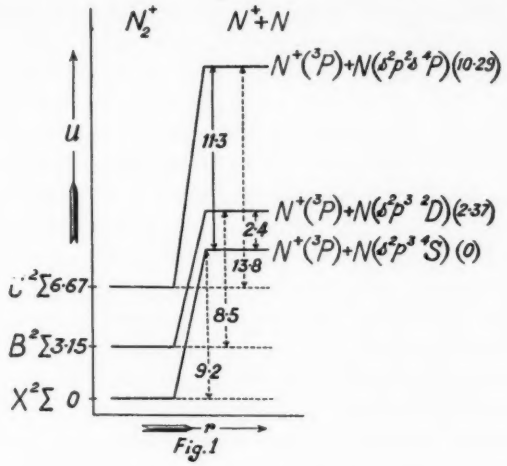

Fig. 1

These are the configurations in their energetical order. It follows that the dissociation products of B $^2\Sigma$ are still two atoms which together have five $2p$ electrons, where as those of C $^2\Sigma$ are two atoms possessing four $2p$ and one $3s$ electrons. N^+ has only singlet terms near 2·38 e.v., but these do not yield in combination with N ^4S a molecular doublet term. Therefore the dissociation products of B $^2\Sigma$ will be $N^+ s^2 p^2\ ^3P + N\ s^2 p^3\ ^2D$. The excitation energy of N ^2D is indeed 2·37 e.v.[6] This combination is the same as that which is accepted for the corresponding B $^2\Sigma$ term of CN.

The term C $^2\Sigma$ may dissociate either into N $2s^2\ 2p^3\ ^4S + N^+\ 2s^2\ 2p^2\ 3s$ or into N $2s^2\ 2p^2\ 3s + N^+\ 2s^2\ 2p^2\ ^3P$. But the lowest term of the former combination with excited N^+, *i.e.*, $N^+\ ^3P$, lies at 18·37 e.v.[6] and is therefore too high. On the other hand the lowest term of excited N, which possesses a $3s$ electron is the term ^4P at 10·29 e.v.[6] above the ground level. This is in very good agreement with the extrapolated difference of 11·28 e.v. within the error of this method, and shows that the products of dissociation of the C $^2\Sigma$ term are

$$N\ 2s^2\ 2p^2\ 3s\ ^4P + N^+\ 2s^2\ 2p^2\ ^3P.$$

This correlation shows that in the ground state N_2^+ possesses a double link which is to a certain extent disturbed by the odd p electron. On excitation of this electron to the next orbital as in B $^2\Sigma$, which process does not involve a change of the main quantum number but means only a rearrangement of the l and s vectors, the linkage is slightly

weakened by excitation. If, however, N^+ combines with a N atom in which this odd electron is removed to the next orbit, a molecular term results, *viz.*, C $^2\Sigma$, in which the bond is considerably strengthened. Indeed if this electron would be entirely removed from the atom the molecule would resemble in respect of stability, the molecule CO in which the free valencies of the two atoms just match each other. The molecule N_2^+ therefore furnishes another example in support of the pair-bond theory of valency. A further significance attaches itself to this correlation of the new term C $^2\Sigma$. The rôle of the disturbing electron has been pointed out[7] in many earlier cases where, however, the odd electron always has been, a premoted one. The view of the pair-bond theory though more straightforward was not entirely conclusive, as far as the odd electron was concerned. The decision against the hypothesis of single bonding and anti-bonding electrons was based more on other considerations, *e.g.*, the nonbonding character of the s^2 group in the presence of an excess of bonding electrons, the course of the dissociation energies, etc. The odd electron of N_2^+, *i.e.*, $3s\,\sigma$ $(2p)$ furnishes the first example of a non-premoted electron (which should be bonding in the theory of molecular orbitals), whose excitation to an orbital of higher energy strengthens the bond. This is in direct contradiction with the hypothesis of bonding and anti-bonding electrons and shows that such classification of single electrons according to the orbitals is not possible. The behaviour of N_2^+ indicates that premotion has, on the linkage, only a secondary effect superimposed on the primary one produced essentially by the pairing of electrons.

In the preceeding paper the actual value of D″ (N_2^+ X $^2\Sigma$) has been determined as 6·18 e.v. On the basis of the above correlations, *i.e.*, using the values of the excitation energies of $2p^3$ ^{1}D and $2p^2$ 3s ^{4}P of N (2·37 and 10·29 e.v. respectively[6]) the actual values of the energies of dissociation of the excited terms can now be calculated. In this way D′ (B $^2\Sigma$) is 5·40 and D′ (C $^2\Sigma$ 9·80 e.v. It will be seen that the former is only slightly lower than D″ (X $^2\Sigma$) whereas the latter is indeed very near to that of D″ (CO). In this connection, attention should be directed to the fact, that the electron configurations determined for N_2^+ obviously hold good for CN also. From this it follows, that the spectroscopically known CN molecule possesses a double bond only and a free electron belonging essentially to the N atom. Its chemical formula therefore is C = N −, or in other words it is the radical of the isonitriles. Attempts which have been made to calculate its energy of dissociation from thermochemical data obtained from HCN which definitely contains the − C ≡ N radical or from $(CN)_2$ which probably has it, are therefore not permissible. This radical constitutes a higher electronic term of C = N −

involving a C atom in which one of the 2*s* electrons has been excited to 2*p*, probably a C ^5S atom.*

The disturbing rôle played by the odd electron can also be seen from the dissociation energies of the ground levels of a number of molecules in the neutral and ionised states, derived in the preceding paper. These figures are not obtained by extrapolation but from direct experimental data and represent within a very few tenths of a volt the actual values of D″. They are as follows :—

Molecule	CO	CO^+	N_2	N_2^+	NO	NO^+	O_2	O_2^+	Cl_2	Cl_2^+
D″ (e. v.)	10·45	7·57 or 9·9	7·35	6·18	5·3	9·4 or 13·3	5·05	6·10	2·47	2·2

The values for NO^+ and Cl_2^+ have been calculated in the same way and included for comparison. For CO^+ two values are given, the first referring to $C^+ + O$, the second to $C + O^+$, their respective merits being discussed in the preceding paper. Again for D″ (NO^+), 9·4 e.v., refers to $N + O^+$, and 10·3 e.v., to $N^+ + O$, which is more probable, the odd electron of NO belonging essentially to the N atom. It can be seen that in a molecule which does not possess odd electrons but has a $^1\Sigma$ ground level, like CO, N_2 or Cl_2, the bond is weakened if an electron is removed by ionisation, whereas it is strengthened in those molecules which possess free valencies as NO ($X\ ^2\Pi$) or O_2 ($X\ ^3\Sigma$). The small change for CO, and Cl_2 suggests that in these saturated molecules the ionisation refers to one of the *p*-electrons not taking part in the linkage, which in the separated system form a closed orbital in O and Cl respectively.

The results described in this paper are, to our mind, a further essential proof of the correctness of the pair-bond theory of valency and confirm the conclusions already reached in earlier papers.

* G. Nordheim (*Ann. D. Physics*, 1936, **26**, 258, *cf.* W. Heitler and G. Poschl, *Nature*, 1934, **133**, 833) suggests that the ground level $^2\Sigma$ of CN is brought about by resonance between terms involving N (^4S) + C (^3P) and N (^4S) + C (^5S). Indeed, otherwise according to the Heitler-London theory in which the terms of the separated atoms determine these of the molecule, the ground level of CN or N_2^+ should be the same as that of NO, *i.e.*, $^2\Pi$. It is therefore gratifying to see that the potential curve of $^2\Sigma$ lies, at small internuclear distances, lower than that of $^2\Pi$ on account of strong repulsion brought about by a higher $^2\Sigma$ term. There is, however, no experimental evidence that this involves, to any practical extent, also a hybridisation of the two forms $C = N -$ and $- C \equiv N$. At least in the lower part of the potential curve of $X\ ^2\Sigma$ which is under direct band spectroscopical observation, no strong perturbations, disturbing the positions of the vibrational levels occur, either in CN or N_2^+ and the linear extrapolation for the excitation energy of the dissociation products leads directly to term differences of the separated atoms which are in no way modified.

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GEOMETRICAL INVERSION IN THE ACIDS DERIVED FROM THE COUMARINS.

Part IV. The Behaviour of the Ethers of the *Cis* and *Trans* Acids.

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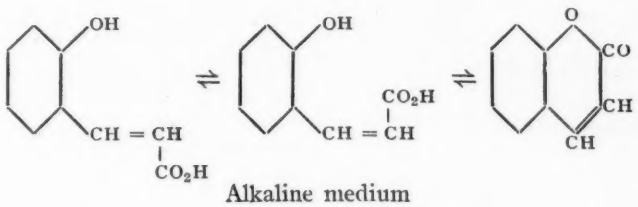
In the previous communications of this series[1,2,3] it has been shown that in the acids derived from the coumarins the change *cis* to *trans* takes place in an alkaline medium only, whereas in neutral or acid medium the tendency is to produce the reverse change. Since normally the *trans* is the stabler form, it was surmised that the abnormal depletion of the *trans* acid is due to the ready conversion of the *cis* form, which may exist in a small proportion, into the coumarin, thereby shifting the equilibrium in the direction of the *cis*. It was only when the formation of coumarin is prevented by the presence of alkali that normal conditions prevail and the *trans* acid is obtained in good yield.

Neutral or acid medium



Alkaline medium

It should be remembered that the presence of an additive reagent is necessary ordinarily, except when light energy or high temperature is made to operate.

It was therefore desirable to study the behaviour of the methyl ethers of the *cis* and *trans* acids, since in them the formation of the pyrone ring should be very difficult. The methyl ethers of the acids from coumarin, 7-methyl-coumarin and 6-nitrocoumarin have been obtained by improved methods and their transformation in neutral, acid and alkaline media studied.

It has been found that irrespective of the nature of the medium the *trans* form is the one favoured. (See the tables below.) If however the conditions facilitate the hydrolysis of the methyl ether group, as when the ethers are heated with concentrated sulphuric acid, coumarin formation takes place.

TABLE I.

Action of Mercuric Compounds.

Methyl ether of	Mercuric chloride in neutral medium	Mercuric acetate in neutral or faintly acid medium	HgO in alkaline medium
1. Coumarinic acid	Complete conversion from *cis* to *trans*	Complete conversion from *cis* to *trans*	Unaffected
2. 4-methyl coumarinic acid	do.	do.	do.
3. 5-nitrocoumarinic acid	Unaffected	Unaffected	Complete conversion from *cis* to *trans* and hydrolysis

TABLE II.

Action of Alcoholic Hydrogen Chloride and Concentrated Sulphuric Acid.

Methyl ether of	Alcoholic HCl product	H_2SO_4 product
Cis acids—		
1. coumarinic acid	*Trans* acid mostly as ester and no coumarin	14% coumarin, 5% *trans* acid and the rest lost
2. 4-methylcoumarinic acid	do.	6% coumarin, 3% *trans* acid and the rest lost
3. 5-nitrocoumarinic acid	do.	70% coumarin, 12% *trans* acid. Rest lost
Trans acids—		
1. coumaric acid	About 80% *trans* ester and rest *trans* acid. No coumarin	2% coumarin, 4% original *trans* acid ether. Rest lost
2. 4-methylcoumaric acid	About 75% *trans* ester and rest *trans* acid. No coumarin	2% coumarin, 3% original *trans* acid ether. Rest lost.
3. 5-nitrocoumaric acid	Completely *trans* ester	5% coumarin, 80% original *trans* acid ether.

The methyl ethers of coumarinic and 4-methylcoumarinic acids undergo inversion easily in neutral and faintly acid media, and their unexpected

failure to do so in the presence of alkali and mercuric oxide may be considered as partly due to the diminished capacity of the mercury compound to attack the double bond under this condition. The inversion of the nitrocoumarinic acid methyl ether in the presence of alkali is accompanied by the demethylation of the ether group. Whether this demethylation is a necessary preliminary is difficult to decide definitely ; but since in neutral medium the compound remains unchanged it may be presumed that in the alkali reaction this factor should have helped the change. Past work has clearly shown that the *cis* hydroxy acids undergo inversion to the *trans* easily in alkaline medium. If the suggestion originally made[4] that amongst the factors determining the facility of geometrical inversion in alkaline solution is to be counted the repulsion between the negative charges of the phenate and carboxylate ions is accepted, we have a rational explanation of the facts recorded above. This driving force does not exist in the methyl ethers and hence the difference in behaviour between the *cis* hydroxy acids and their methyl ethers in alkaline solution.

In the presence of alcoholic hydrogen chloride the ethers of the *cis* acids undergo inversion into the *trans* compounds and at the same time get esterified to a great extent. The *trans* acid ethers under the same conditions remain unchanged except for the esterification of the carboxyl group.

Concentrated sulphuric acid at 100° introduces a different type of conditions mainly due to its capacity as a demethylating and sulphonating agent. This explains the formation of coumarins from the methyl ethers and the considerable loss of material by the formation of soluble sulphonic acids. The *cis* acid ethers give both the *trans* acid ethers and the corresponding coumarins. The inversion to the *trans* compounds may be considered to be the normal change whereas the formation of coumarins is due to demethylation. In the case of the ether of the nitro-acid chances of demethylation are greater and sulphonation far less and hence such a large formation of the nitrocoumarin and so little loss.

Experimental.

Preparation of the required methyl ethers.

Methyl ether of coumarinic acid.—Attempts to prepare it by methylating with dimethyl sulphate a solution of coumarin in aqueous sodium hydroxide were without success, coumarin being recovered unchanged. It was however easily obtained by the method of Perkin[5] (see also Simonis[6]) in which a methyl alcoholic solution of coumarin is treated with sodium methylate and methyl iodide. It crystallised out of alcohol as glistening monoclinic crystals, melting at 91–92°.

Methyl ether of coumaric acid.—It was noticed that the method detailed in Simonis's book, *Die cumarine*, p. 87 (see also Reychler[7]) failed to give satisfactory results since mostly the ether of the *cis* acid was obtained. If however it is modified by heating the mixture of coumarin and sodium methoxide in dry alcohol for about 4 hours under reflux before treating with methyl iodide, a good yield of the ether of the *trans* acid is obtained. The preparation is markedly influenced by the presence of moisture in the alcohol.

This ether was readily obtained by methylating coumaric acid with dimethyl sulphate in the presence of sodium hydroxide. Coumaric acid was dissolved in excess of aqueous alkali and shaken with two equivalents of dimethyl sulphate for half an hour (gradual addition). It was finally heated on the water-bath for 1 hour and the ether percipitated with acid. It recrystallised from dilute alcohol as colourless narrow plates and prisms melting at 185–86°.

4-*Methyl coumarinic acid methyl ether* was obtained from 7-methyl coumarin by following the same procedure as for the ether of coumarinic acid. When crystallised from alcohol it came out as colourless stout rhombic prisms melting at 160–61°. [Found : C, 68·4%; H, 5·9%; $C_{11}H_{12}O_3$ requires C, 68·7%; H, 6·3%. Found in the silver salt : Ag, 35·9%; $C_{11}H_{11}O_3Ag$ requires Ag 36·1%.]

4-*Methyl coumaric acid methyl ether.*—4-methyl coumaric acid was obtained from 7-methyl coumarin by the method of Seshadri and Suryaprakasarao[2] and was methylated by means of dimethyl sulphate and sodium hydroxide as detailed in the case of coumaric acid methyl ether. It crystallised from aqueous alcohol as long narrow rectangular plates melting at 209–10°. [Found : C 68·3%; H, 6·0%; $C_{11}H_{12}O_3$ requires C, 68·7%; H, 6·3%. Found in the silver salt : Ag, 36·6%; $C_{11}H_{11}O_3Ag$ requires Ag, 36·1%.]

5-*Nitrocoumarinic acid methyl ether.*—Direct methylation of 6-nitrocoumarin in alkaline solution with dimethyl sulphate could not be effected. The compound was therefore obtained from 6-nitrocoumarin by following the procedure of Clayton.[8] The nitro-coumarin was converted into the di-silver salt of the coumarinic acid, from which the ether ester was made by the action of methyl iodide, and this on hydrolysis gave the required compound crystallising from alcohol as colourless needles melting at 202–3° C. It was noticed that Clayton's method of hydrolysis using boiling alcoholic sodium hydroxide gave rise to an impure product (probably due to demethylation) and considerable loss of material was sustained during the purification. The best procedure was to effect the hydrolysis with 5% aqueous potash, kept

boiling till a clear solution was obtained (5 minutes), cooling the solution and acidifying. The yield was almost quantitative and the product was readily obtained very pure by a simple crystallisation from alcohol, m.p. 202–3°.

5-*Nitrocoumaric acid methyl ether*.—(i) Direct methylation of 5-nitrocoumaric acid was not successful.

(ii *a*). 5-Nitrocoumaric acid[2] was converted into the di-silver salt as given below and this made to react with methyl iodide in ether solution. By this method was obtained the methyl ether of methyl 5-nitrocoumarate which was found to have the properties described by Clayton[8] for the compound which he obtained from 5-nitrocoumaric acid methyl ether through the silver salt.

5-Nitrocoumaric acid (21 g.) was dissolved in sodium hydroxide (8 g.) and treated with silver nitrate (35 g.) dissolved in water. The reddish silver salt was filtered, washed and dried on a porous tile in vacuum.

The dry silver salt (16 g.) was shaken with methyl iodide (16 g.) and ether (100 c.c.) for two hours. The residue left after evaporating off the ether, was then extracted with hot alcohol and the solution allowed to crystallise. The ether ester was obtained as colourless needles, m.p. 163° in a yield of about 70%.

(ii *b*). Methyl 5-nitrocoumarate[1] was methylated with methyl iodide and potassium carbonate in acetone solution.

Methyl 5-nitrocoumarate (5 g.) was dissolved in acetone (150 c.c.), dried over potassium carbonate and gently boiled with excess of methyl iodide (5 c.c.) and anhydrous potassium carbonate (10 g.) for 4 hours. Most of the acetone was then distilled off and the residue treated with water and acidified. The solid that separated was filtered, washed and recrystallised from alcohol, m.p. 163°. The yield was about 80%.

The *trans* ether ester was hydrolysed with hot 5% aqueous potash as in the case of the *cis* compound. (Stronger alkali and prolonged heating resulted in the hydrolysis of the ether group also. Both cold and hot alcoholic potash were unsatisfactory.) The product was obtained very pure by one crystallisation from alcohol, m.p. 236° and the yield was almost theoretical.

Action of mercury compounds on the ethers of the cis *acids. Mercuric oxide* (*alkaline medium*).—Solutions of the *cis* acid ethers in excess of aqueous potash were shaken with yellow mercuric oxide for about half an hour, filtered and the product precipitated with hydrochloric acid and examined. If cold treatment was ineffective the solution was boiled for 3 to 5 hours, filtered

and the products examined. If there should have been any mercuration the mercury was removed with hydrogen sulphide in an alkaline solution.

Coumarinic acid methyl ether and 4-methyl coumarinic acid methyl ether were unaffected by treatment in the cold. On boiling however mercurated products were produced which gave the original *cis* compounds on decomposition with hydrogen sulphide. No inversion seemed, therefore, to take place in these cases. 5-nitrocoumarinic acid methyl ether underwent complete isomerisation into the *trans* form without any mercuration, on boiling with mercuric oxide and aqueous alkali; but at the same time it got demethylated with the result that the final product was an impure mixture. Prolonged boiling, however, gave pure 5-nitrocoumaric acid.

Mercuric Chloride (*neutral medium*).

The ether of the *cis* acid (1 g.) and mercuric chloride (2 g.) were dissolved in sufficient quantity of 50% aqueous alcohol and boiled for 2 to 3 hours at the end of which enough hydrochloric acid was added to make the strength 1% and allowed to cool. If no change was effected by this treatment, a simple aqueous solution of mercuric chloride was used and the boiling continued for 6 hours.

The methyl ethers of coumarinic and 4-methyl-coumarinic acids were easily converted into the *trans* ethers in good yield, whereas the ether of 5-nitrocoumarinic acid was unaffected in aqueous-alcoholic or aqueous medium.

Mercuric acetate (*neutral or weak acid medium*).

The ether of the *cis* acid was dissolved in aqueous sodium hydroxide, neutralised with acetic acid and then treated with an aqueous solution of mercuric acetate slowly with stirring. The bulky precipitate that was produced was filtered off after an hour, dissolved in aqueous caustic soda and saturated with hydrogen sulphide. After filtering off mercuric sulphide, the filtrate was acidified and the product examined after crystallisation from alcohol, if necessary.

The ethers of coumarinic and 4-methyl-coumarinic acids gave good yields of the *trans* isomers, whereas the ether of 5-nitrocoumarinic acid was unaffected. This nitro acid was also treated with boiling methyl alcoholic mercuric acetate. The reaction was very slow and the product did not yield the pure *trans* acid though it had undergone some change.

Action of alcoholic hydrogen chloride on the ethers of the cis *acids.*

The ether was dissolved in sufficient quantity of anhydrous alcohol, saturated with dry hydrogen chloride at 0° and allowed to stand for 24 hours

at room temperature. It was then refluxed for 2 hours, most of the alcohol distilled off, the residue treated with water and ether-extracted. The ether solution was then shaken with small volumes of aqueous sodium carbonate in order to remove the acid portion and then washed with a small volume of water. After drying over anhydrous calcium chloride it was evaporated in a tared flask and the neutral residue weighed and examined. The carbonate solution was acidified, ether-extracted and the acid portion obtained and examined separately.

The ether of coumarinic acid was completely converted into the *trans* form and most of it (about 80%) esterified. On hydrolysing the neutral portion pure ether of the *trans* acid was obtained in good yield and no coumarin could be detected. The acid portion was pure *trans* acid ether (10–15%).

The methyl ether of 4-methyl-coumarinic acid gave rise to a complex neutral product with dry alcohol saturated with hydrogen chloride. It contained however no coumarin. On hydrolysis it gave rise to an acid which could not be obtained pure. On using however aqueous alcohol (1 : 1) containing hydrochloric acid (3 c.c. of concentrated acid in 40 c.c. of the mixture) it smoothly underwent inversion giving mostly the ester of the *trans* acid ether.

The ether of 5-nitrocoumarinic acid was almost completely esterified and simultaneously transformed into the *trans* form. Methyl ether of ethyl 5-nitro-coumarate, m.p. 85° (Clayton[8]) was obtained (80–85%) and yielded on hydrolysis the ether of the *trans* acid. No coumarin could be detected.

Action of alcoholic hydrogen chloride on the ethers of the trans *acids.*—

The same procedure as with the *cis* ether was adopted. The ether of coumaric acid underwent conversion into the ester to about 80%. No further change could be noted and no coumarin was formed.

In the case of the ether of 4-methyl-coumaric acid, 25% of the acid was recovered unchanged and the rest was found to be an ester free from 7-methyl coumarin. But on hydrolysing the ester, the acid that was obtained could not be purified or characterised. It seemed to have undergone some complex changes. This did not happen if aqueous-alcoholic hydrochloric acid was employed. The *trans* acid ether was unchanged except for partial esterification.

The methyl ether of 5-nitro-coumaric acid with methyl alcohol as the solvent was converted almost completely into a neutral compound melting at 162° and found to be identical with the methyl ester of the original *trans* acid.

Action of concentrated sulphuric acid.

On the cis *ethers.*—The compound (1 g.) was treated with concentrated sulphuric acid (10 c.c.) and heated at 100° for one hour. It was then cooled, poured into cold water (100 c.c.) and the product worked up in the same way as was adopted with alcoholic hydrogen chloride.

The methyl ether of coumarinic acid gave 14% coumarin; about 5% of the corresponding *trans* acid could be isolated and the rest was lost by sulphonation. From the ether of 4-methylcoumarinic acid only 6% yield of 7-methyl-coumarin could be obtained, along with 3% of the ether of the *trans* acid; the rest was lost. The ether of 5-nitrocoumarinic acid gave about 70% of 6-nitrocoumarin and about 12% of the *trans* acid ether; the rest was lost.

On the trans *ethers.*—The same procedure as described above was adopted. The methyl ethers of coumaric and 4-methyl-coumaric acids gave about 2% yield of the corresponding coumarins. Only 3 to 5% of the unchanged acids were recovered and the rest was lost. From the ether of 5-nitro-coumaric acid was obtained about 5% yield of 6-nitrocoumarin and about 80% of the original *trans* acid ether was recovered unchanged.

Summary.

The methyl ethers of the *cis* and *trans* acids from coumarin, 7-methyl-coumarin and 6-nitrocoumarin have been obtained by improved methods and their transformation in neutral, acid and alkaline media studied. It has been found that irrespective of the nature of the medium the *trans* form is the one favoured, thereby showing that the unusual depletion of the *trans* hydroxy acids (coumaric acids) in neutral and acid media is due to the ready formation of coumarins from the corresponding *cis* acids, which may exist in small proportions in equilibrium with the *trans*. This ring closure is prevented in the methyl ethers. If however conditions favour the hydrolysis of the ether group as when the compounds are heated with concentrated sulphuric acid coumarin formation takes place to some extent.

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GRAVITY, GEOID AND PLUMB-LINE DEFLECTIONS IN MOUNTAINOUS AREAS.

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1. *Introduction and brief historical development of the idea of mountain compensation.*—It is now an accepted fact that the larger features of visible topography are compensated in some form or other. In 1854, Pratt published a paper in *Philosophical Transactions of the Royal Society*, in which he calculated the Himālayan attraction at three stations of the Great Arc. He found the deflections to be greater in amount than the observed values. This led him to formulate his theory of compensation, namely, that the irregularities of mountain surfaces have arisen from the vertical expansion of the earth's crust from depths below, which has resulted in the density underneath being less, so that it counteracts the effect of visible masses. Helmert in 1890 in his pamphlet "Die Schwerkraft in Hochgebirge" discussed the subject of mountain compensation with the meagre data at his disposal. He utilised 14 Alpine gravity stations observed by Von Sterneck in 1887, and some Himālayan stations observed by Captains Basevi and Heaviside during the years 1864-74. (These Indian stations have since been found to be of no value, as no flexure correction was applied to them.) Helmert concluded that when the values of gravity on mountains were corrected for the attraction of visible masses, they pointed to a subterranean mass-defect.

These pioneers were handicapped by the fact that they had not enough observational data at their disposal. Considerable work has been done since their time, and it is the object of this paper to discuss data bearing on mountain compensation in different parts of the world. The question whether geoid follows topography in mountainous areas is also considered.

2. *Practical methods of arriving at numerical estimates of compensation.*—Hayford[1] in 1909 gave a practical shape to Pratt's theory of compensation, and published tables, by which the effect of topography and compensation on the gravity and plumb-line deflection at a station could be computed. The magnitude of these residuals enables one to see, to what extent his compensation hypothesis succeeds in explaining the observed facts.

Hayfordian hypothesis cannot, however, be mechanically true, as it assumes point to point compensation, which implies that the earth's crust

offers no resistance to deformation. Besides, this hypothesis is ontradicted the crustal conditions as deduced from the seismological evidence, namely, by that the crust is composed of three layers of discontinuity.

A more rational hypothesis appears to be to assume the topographic inequalities to be compensated regionally.

V. Meinesz,[2] assuming the earth's crust to behave like an infinite elastic plate of constant thickness 25 km. floating over a magma, whose density is greater than it by 0·63, and deformed by the weight of the topographical masses, considered three cases :—

(*a*) Crust is of constant density, and compensation is concentrated at the junction of the crust with the magma.

(*b*) Compensation is uniformly distributed throughout the 25 km. depth.

(*c*) Compensation is concentrated at the upper surface of the crust, and is due to elastic deformation of the crust due to loading.

This corresponds to the usual Free-air anomaly improved by the considerations of elasticity of the earth.

Heiskanen[3] has brought out tables for Airy's hypothesis of compensation assuming the thickness of the crust corresponding to zero elevation of a region to be 40, 60, 80 and 100 km., and to be constant in all parts of the earth. In this hypothesis, the crust is supposed to be floating over a magma of higher density.

Seismological evidence shows, that the normal structure of the crust is by no means homogeneous, but consists of 3 layers possessing different physical properties. The interfaces of these layers according to Jeffreys[4] are 10 kms. and 30 kms. below sea-level. Considerable progress[5] has been made by starting with the above as normal structure of the earth, and assuming the Δg's to arise from crustal warping.

Yet another and a very powerful method of getting at the subterranean mass-anomalies is by the computation of the shape of the geoid, given sufficient number of meridional and prime vertical deflections. These deflections are integrated along meridians and parallels[6] and the separation of the geoid from its reference spheroid determined. If we do the same with the Hayford residuals, we get the compensated geoid,[7] which is a level surface of the anomalies from Hayford's hypothesis. The undulations of these geoids yield very comprehensive information about the nature of compensation in an area.

3. *Details of gravity stations in the Himālayas and the anomalies there.*— The Free-air, Bouguer and Hayford anomalies at all the pendulum stations in India are tabulated in *Geodetic Report*, Vol. VI—Supplement and its

addenda in the annual Geodetic Reports. In order to get more information about the nature of compensation under the Himālayas, anomalies at the Himālayan stations were computed according to the three hypotheses of V. Meinesz, and also according to Airy hypothesis assuming the thickness of the crust to be 40 kms. Table I gives the anomalies for stations in the Kashmīr area. The remaining mountainous stations are shown in Table II. Table III gives the anomalies at the three stations Darjeeling, Kurseong and Sandakphu, which lie practically on the same meridian. The means with and without regard to sign are given in Table I. The ranges of the various anomalies are also shown in a tabular form.

TABLE I.

Serial No.	Station	Height	Δg_A	Δg_B	Δg_C	Airy	s_1	s_2	s_3
		Feet	cm./sec.^{2}	cm./sec.^{2}	cm./sec.^{2}	cm./sec.^{2}	cm./sec^2	cm./sec.^{2}	cm./sec.^{2}
1	Murree ..	6885	+·032	−·184	−·025	−·027	−·024	−·033	−·044
2	Domel ..	2239	−·167	−·227	−·048	−·025	−·012	−·015	−·021
3	Shādipur ..	5193	−·116	−·286	−·030	−·017	+·007	+·005	+·004
4	Gandarbāl ..	5200	−·094	−·261	+·010	+·023	+·044	+·048	+·048
5	Hayan ..	6084	−·105	−·281	+·017	+·021	+·043	+·049	+·051
6	Sonāmarg ..	9050	−·013	−·296	+·043	+·078	+·064	+·073	+·079
7	Churawan ..	8151	−·056	−·306	+·032	+·038	+·059	+·066	+·070
8	Minmarg ..	9351	−·033	−·324	+·035	+·040	+·060	+·069	+·074
9	Deosai I ..	13311	+·146	−·298	+·090	+·094	+·131	+·141	+·149
10	Deosai II ..	12805	+·094	−·332	+·062	+·065	+·104	+·115	+·122
11	Deosai III ..	12391	+·111	−·301	+·095	+·100	+·138	+·149	+·156
12	Lālpur ..	5633	−·045	−·230	+·017	+·037	+·051	+·051	+·049
13	Srīnagar ..	5198	−·070	−·240	+·021	+·034	+·053	+·055	+·055
14	Pingalan ..	5227	−·073	−·245	+·012	+·030	+·041	+·043	+·042
15	Yūs Maidān ..	7867	+·024	−·234	+·008	+·006	+·016	+·014	+·011
16	Korag ..	10952	+·149	−·205	+·034	+·037	+·031	+·029	+·025
17	Tosh Maidān ..	10315	+·135	−·198	+·050	+·050	+·055	+·051	+·027
Mean without regard to sign =			·086	·262	·037	·042	·055	·059	·060
„ with „ „ =			−·005	−·262	+·025	+·034	+·051	+·054	+·053

TABLE II.

Serial No.	Station	Height	Δg_A	Δg_B	Δg_C	Airy	s_1	s_2	s_3
		Feet	cm./sec.^{2}	cm /sec.^{2}	cm /sec.^{2}	cm./sec.^{2}	cm./sec.^{2}	cm./sec.^{2}	cm./sec.^{2}
1	Dehra Dūn ..	2239	−·074	−·145	+·006	+·014	+·017	+·008	−·002
2	Mussoorie .. (Camel's Back)	6924	+·085	−·123	+·053	+·054	+·065	+·058	+·048
3	Simla ..	7043	+·091	−·130	+·036				
4	Kālka ..	2202	−·034	−·104	+·018	Regional anomalies for these stations cannot be readily computed			
5	Mohan ..	1660	−·070	−·123	+·003				
6	Asarori ..	2467	−·050	−·131	+·004				
7	Kālsi ..	1684	−·073	−·120	+·033				
8	Rājpur ..	3321	−·040	−·143	+·026	+·019	+·033	+·027	+·018
9	Chakrāta ..	6933	+·096	−·125	+·066	+·069	+·074	+·068	+·060
10	Darshani ..	3996	−·059	−·187	+·029	+·066	+·045	+·043	+·038
11	Kumaria ..	1866	−·095	−·151	−·008	+·069	−·004	−·014	−·026

TABLE III.

Serial No.	Station	Height	Δg_A	Δg_B	Δg_C	Airy	s_1	s_2	s_3
		Feet	cm./sec.^{2}	cm./sec.^{2}	cm./sec.^{2}	cm./sec.^{2}	cm./sec.^{2}	cm./sec.^{2}	cm./sec.^{2}
1	Darjeeling ..	6966	+·055	−·154	+·032	+·035	+·049	+·044	+·036
2	Kurseong ..	4913	·000	−·147	+·010	+·010	+·026	+·016	+·005
3	Sandakphu ..	11766	+·189	−·155	+·048	+·048	+·056	+·053	+·047

Range of Table I.

Δg_A	Δg_B	Δg_C	Airy	s_1	s_2	s_3
−167 to +149 = (316)	−184 to −332 = (148)	−48 to +95 = (143)	−27 to +100 = (127)	−24 to +138 = (162)	−33 to +149 = (182)	−44 to +156 = (200)

Range of Table II.

+96 to −95 = (191)	−123 to −187 = (64)	−8 to +66 = (74)	+14 to +69 = (55)	−4 to +74 = (78)	−14 to +68 = (82)	−26 to +60 = (86)

Range of Table III.

0 to +189 =(189)	−147 to −155 = (8)	+10 to +48 = (38)	+10 to +48 = (38)	+26 to +56 = (30)	+16 to +53 = (37)	+5 to +47 = (42)

We see that Free-air reduction is hopeless. Bouguer is consistently negative indicating the presence of compensation. Mean Hayford anomaly in Table I is about 1/10th of Bouguer. A point of interest is, that while Δg_A's are very ragged, the improved Free-air anomalies s_3 are much more smooth. Thus, for the three stations of Table III, Δg_A shows a large range of 189 mgals, while the range of s_3 is only 42 mgals. It has been suggested that using Hayford's hypothesis, one should expect to get positive Δg_c's at mountainous stations and negative Δg_c's in valleys. The reason for this is, that the actual compensation is more nearly regional than local, which means that in Hayford's hypothesis, one assumes too great a depth of compensation under the mountains. A glance at Table I shows, that indeed nearly all Δg_c's in the Himālayan region are positive. In the mountainous central part of U.S., Δg_c's are also all positive, and the greater the height of the station, the more positive are the anomalies. This is remarkably true for Himālayan stations as well, and at first sight, one would be inclined to say, that this was a distinct proof of compensation being regional. It was therefore expected that Airy's or some other hypothesis of regional compensation would give smaller residuals than Hayford's hypothesis. But even a cursory glance at the tables shows, that none of these hypothesis is an improvement on Hayford's. It thus appears to be a merit of Hayford's hypothesis, that although it is not true to nature, it gives practically the same result as regional compensation. In outer zones in particular, Hayford's reduction corresponding to a depth of compensation $2d$ is almost identical with Airy's reduction corresponding to average depth of compensation d.

4. *Compensation of the Himālayas and the Alps.*—From a discussion of the gravity and plumb-line deflections in the Himālayan region, Burrard[8] came to the conclusion, that in India there are very important sub-crustal features, which modify greatly the effect of the Himālayas. He pointed

out the existence of a "Hidden Range" running east and west in Central India, and found gravity to be in defect in the Sub-Himālayan region, indicating over-compensation there. The existence of both these features has been confirmed by modern work. Chart XIV, *Geodetic Report*, Vol. V, gives a set of mass-anomalies, which would produce the compensated geoid in India. The above features are shown very well by this chart. Again from the Isostatic gravity anomalies in India, a distribution of mass-anomalies expressed as a coating of normal crustal density on the reference surface has been determined.[9] It is shown that the Gangetic plain is an area of underload, the deficiency being equivalent to a skin density of -500 to $-2{,}000$ feet of rock condensed on the spheroid.

The gravity stations in the Himālayan region have already been given in § 3. We have seen, how Hayford's, Airy's and V. Meinesz's hypotheses give much smaller average residual than Bouguer. In particular, Hayford anomaly is 1/10th of Bouguer, and we can say, that the compensation is almost complete under the Himālayas. To the north of Kashmīr, we have Δg_c at Depsang as -64 mgals, and at Yārkand -57 mgals, indicating that Kara-korum is over-compensated.

In addition to the above gravity data, valuable information is available from the meridional deflections which have been observed along two lines in the Himālayas, one from Pīr Panjāl to Skārdu in Kashmīr, described in *Geodetic Report*, Vol. III, p. 80, and the other through the mountainous country between latitudes $32\frac{1}{2}°$ and 34°, described in *Geodetic Report*, Vol. VII, p. 54.

In *Geodetic Report*, Vol. III, an oblique section is drawn from Ranjitgarh to Skārdu, and compensated geoid is obtained by integrating Hayford's anomalies along this line. There is however an element of uncertainty about this section in that only meridional deflections are available, and for drawing the section, it is assumed that the total deflections are at right angles to the line of the hills. Chart X, *Geodetic Report*, 1935, gives compensated geoid with respect to the International spheroid and shows the whole of North India to be an area of defect, while Δg's with respect to both Helmert and International spheroids have positive values round about Kashmīr, indicating some excess mass there.

In *Geodetic Report*, Vol. III, it is discussed how this discrepancy can be reconciled. Some more observations are however needed to clear up the issue.

Bearing on this question, the results of the scientific work of the Nanga Parbat Expedition will be very valuable. A preliminary account of this

work is published by Finsterwalder in "Wissenschaftlichen Arbeiten des Geodatisches Institutes der Technischen Hochschul, Hannover." Meridional deflections have been determined at 15 stations, but no account seems to have been published yet about the deflections obtained there. Height adjustment showed, that at Astorost, which is about twenty miles to the east of Nanga Parbat, there is a large deflection to the east away from the massif, which indicates that Nanga Parbat is over-compensated. Nanga Parbat is about 2,000 metres higher than its surroundings, so one would expect plumb-line deflections to point towards it. But in this case it is pointing directly away, indicating a zone of large mass-defect, *i.e.*, over-compensation.

More definite conclusions will however be drawn, when the section of the geoid will be available in this area.

In the Alps, gravity stations are in great abundance, and an excellent attempt to decide the question of local *versus* regional compensation is that of Miss Lehner. ("Beit. zur Untersuchung der Isost. Kompensation der Schweirischen gebirg-massen," *Verh. der Naturf. gesselschaft in Basel*, Vol. XLI.) Miss Lehner excluded from her investigation, the north and south portions of the Alps, where Bouguer and Isostatic anomalies are considerable, and considered 191 stations in the central region of the Alps. Generalising the topography in various ways, and assuming different depths of compensation, Miss Lehner concluded that regional compensation on Pratt's hypothesis with a depth of compensation of 100 kms. gives gravity in the central portion of Swiss Alps with a probable error of 8 mgals. Region in independent equilibrium has an area of at least 4,000 square kms. Computations are rather laborious, and Miss Lehner has only treated the Pratt's hypothesis and not the Airy one, so that it cannot be said, which hypothesis fits better.

An interesting fact has been brought to light by Heiskanen[10] about the compensation of the Alps. In the ordinary way, geologists affirm that mountain chains and the valleys are compensated regionally as a whole, which means that the mountain chains are under-compensated, while the valleys are over-compensated. In the case of the Alps, Heiskanen finds that the gravity anomalies in the marginal depressions of the Alps have larger positive values than those in the Alps themselves, which is contrary to the above. Marginal depressions of the Alps appear to be over-compensated as compared to the Alps themselves, *i.e.*, Alps considered as one whole with their valleys are not compensated.

5. *Geoid and the surface configuration.*—We will now answer the important question, "Does the natural geoid tend to follow the surface configuration?" There are several plane areas, in which the geoid neither follows

the topography, nor the local geology. One such example is the extensive region of the "Hidden Range" in India, in which the geoid shows a rise of 25 feet, which cannot be due to the visible topography. The Hayford gravity anomalies in this region are also systematically positive. Another region where the subterranean features have shown themselves strikingly is that of the waters of the East Indian Archipelago. In the ocean deeps, V. Meinesz found Δg_c's to be strongly negative, and in their vicinity strongly positive. In areas of moderate topography, then, it may happen that the subterranean features may play the dominant part. It would be of interest to see, whether there are cases of a depressed geoid under a mountainous region. It has been argued[11] that Stokes' formula indicates that geoidal rise is due to gravity anomalies all over the globe, and so it is possible to have a depressed gecid associated with local excess of gravity. Gravity anomalies refer to an " Earth spheroid ", whose centre of gravity and minor axis coincide with that of the earth. Geoidal elevations and plumb-line deflections refer to a geometrical " reference spheroid ", which is generally taken to be a spheroid of best fit to the limited region. The minor axis of this spheroid is parallel to that of the earth.

An " Earth spheroid " is useful, when we are considering the earth as a whole. In dealing with the effects of mass-anomalies in limited areas, it is preferable to use the reference spheroid. It can be shown, that if Δg's contain harmonics of lower order, the geoid will have fairly large undulations due to these, and therefore the " Earth spheroid " would not give a good picture of the local undulations. The best fitting " reference spheroid", on the other hand, would mask the general effect due to the remote portions and would show the local features of the geoid. Hence, by choosing a suitable reference spheroid, we can so arrange, that on the average depressed geoid is associated with negative Δg's.

The question, which we want to answer, however, is " Are there any mountain regions of the globe, which are over-compensated to such an extent, that the geoid is depressed there ?" The following examples serve to give an idea of the amount of over-compensation needed to do this. Consider the rise of the geoid due to compensated topography of height 5 kms. in Hayford's zone A — J. By Lambert's[12] tables,

$$N_T = (42{\cdot}3 + 31{\cdot}4 + 63{\cdot}2 + 81{\cdot}5) \times 2{\cdot}67 = 583{\cdot}1 \text{ cms.}$$

$$N_c = (42{\cdot}3 + 31{\cdot}4 + 63{\cdot}2 + 81{\cdot}5 + 121{\cdot}3 + 124{\cdot}3 + 319{\cdot}2 + 528{\cdot}7) \times (-0{\cdot}119) = 156{\cdot}1 \text{ cms.}$$

Rise = 427 cms. Let y be the density of over-compensation, which will neutralise this. Then $y \times 1311{\cdot}9 = 427$, or $y = 0{\cdot}3$. Therefore an

over-compensation of 11 per cent. will remove N. If the topography be of height 2 kms. only, then the amount of over-compensation needed is 6 per cent.

Reverting now to the question in hand, we will consider the course of the geoid in some mountainous regions of the globe.

In his article on "The African Arc of Meridian" in *South African Journal* McCaw has drawn a section of the geoid along the arc in Rhodesia. Geoid rises under Drakensberg Range, and falls under Zambesi valley. There is under-compensation in this area, because he says that elevations and depressions are so marked that even if Isostasy is allowed for, compensated geoid would also tend to follow the surface configuration.

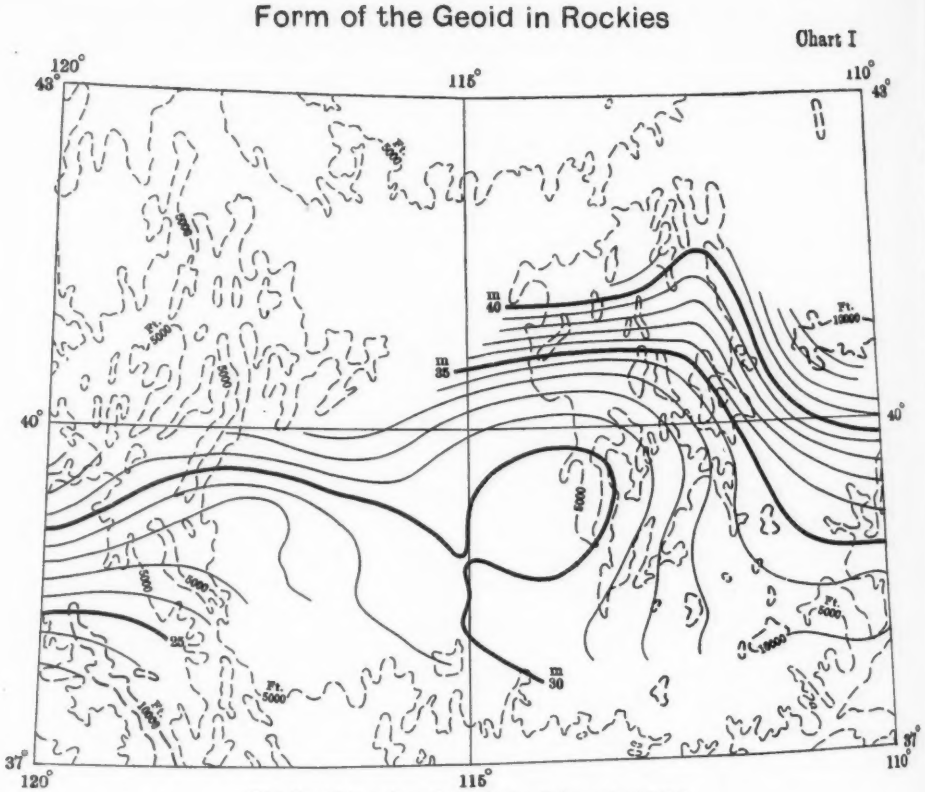
In the case of India, evidence so far is, that the Himālayas are under-compensated. Gravity anomalies at most of the Himālayan stations are positive. Chart IX, *Geodetic Report*, 1935, shows that geoid is elevated under the mountains. *Geodetic Report*, VII, Plate VI, suggests that geoid may be depressed to the north of Skārdu, but more observations are needed to confirm this.

In Central Rājputāna, there is the Arāvalli Range of moderate height 2,000 ft. Chart IX of *Geodetic Report*, 1935, shows, that the geoid there is more elevated than the neighbouring region. This region is generally elevated on account of the " Hidden Range ", but the secondary effect of Arāvallis is quite clear. Further evidence is afforded by Plate XII, *Geodetic Report*, 1933, where the geoid rises under the Chin Hills and Shan Plateau. In Plate XXI of *Geodetic Report*, 1934, the geoid shows an elevation under the Palni Hills and Mysore Plateau, and in Chart VI of *Geodetic Report*, 1935, it shows a steady rise from Sibi to Quetta closely following the topography.

Geoid in Rockies.—Looking at Chart No. 17 of " The Figure of the Earth and Isostasy from Measurements in U. S., " we see that along the meridians of 110° and 115°, and along the parallel of 40°, the geoid is well above the reference spheroid.

Between latitude 40° to 41° and longitude 110° to 111°, geoidal rise varies between 40 and 44 metres. This area is covered by one of the greatest of mountain masses in U. S. Chart I gives the topographical and geoidal rise in this area.

Geoid in Harz.—Another mountainous region, in which the geoid is known with extraordinary precision is that of Harz Mountain in North Germany. These mountains are not very high, the peaks being 600 metres or so. If there were over-compensation here, it could easily mask the effect of these mountains.



The Geoid is referred to Clarke Spheroid of 1866.
(*Copied from Chart No. 17 of "The Figure of the Earth and Isostasy from Measurements in the United States" by John F. Hayford, 1909.*

An account of the plumb-line deflections and gravity in this area is given in detail by Prof. Galle in *Ver. des Konige Pruz. geod. Inst. N. F. 61.* The contours of the geoid are drawn in Tafel V. The rise of the geoid is about 4 metres in this area, and it is more under the mountainous part. Hence in this area, the geoid follows topography.

Geoid in St. Gotthard's Meridian.—In this meridian also, the geoid is known with great accuracy. The observations and computations have been carried out with a precision, which leaves nothing more to be desired. Between latitudes 47° 48′ and 46° 7′, a series of 54 stations was observed by Astrolabe on St. Gotthard's meridian. Deflections at 57 intermediate points were then determined by interpolationg the deflection anomalies at the 54 stations

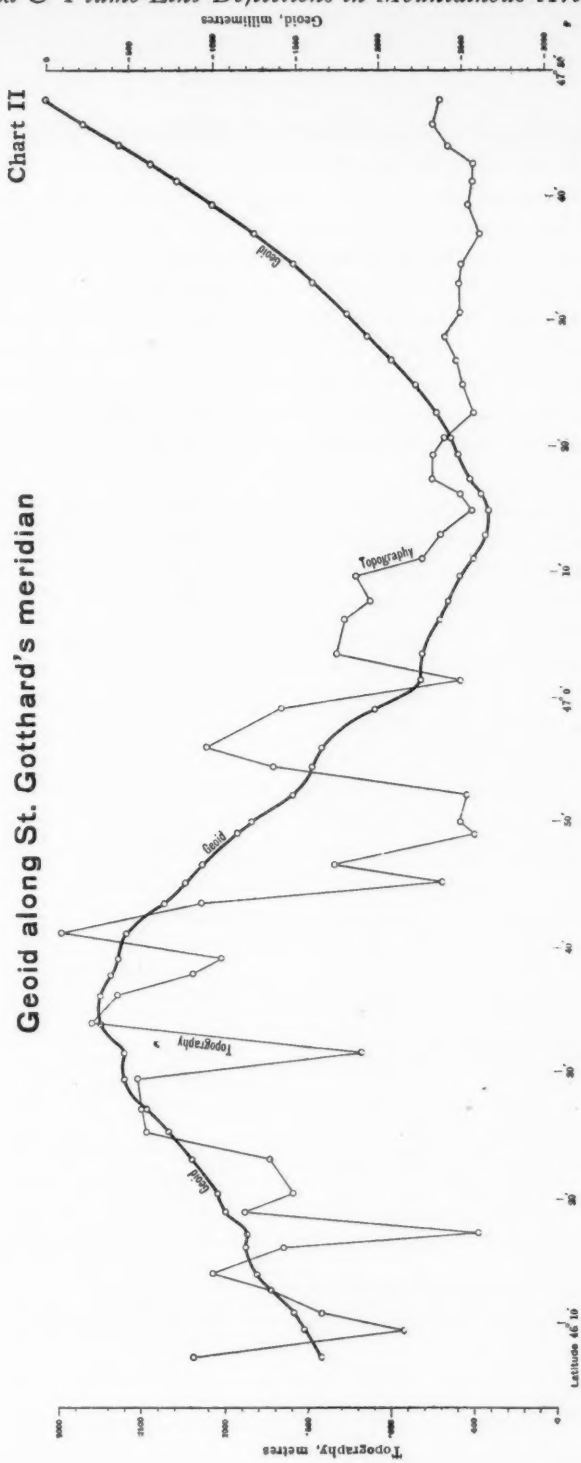


Chart II
Geoid along St. Gotthard's meridian
Geoid, millimetres
Topography, metres
Latitude 46° 10'
47° 0'
Geoid
Topography
Geoid
Topography
Geoid

of observation, and adding Hayford deflections to them. The density of the points is therefore one per mile.

Chart II shows the section of the geoid drawn with the help of the data published in *Proces-Verbal de la 81 me. sèance de la commission géodésique suisse*, 1935, by Dr. E. Hunziker. The maximum range of the geoid in this region is about 8 ft., so the spheroid chosen fits the area well. Maximum depression of the geoid is under Zurich sea, and the maximum elevation under St. Gotthard massif. Hence, in this area, the natural geoid follows topography remarkably well.

With the evidence available so far, it thus appears to be a safe statement to make, that in mountainous regions, the geoid follows the topography on the whole.

6. *Summary.*—Gravity anomalies at stations in the Himālayan region have been determined with four more hypotheses besides the usual Hayford's. Results indicate, that Hayford's hypothesis gives smaller residuals than the regional hypotheses of V. Meinesz and Airy, although these latter hypotheses are more logical. It appears that departures in nature from any form of Isostasy are much greater than the differences between the various systems.

Some of the mountainous regions of the globe, for which geoidal contours are known, are considered to see if there are any cases, in which depressed geoid is associated with an elevated region. If the geoidal elevations are taken with reference to the spheroid fitting best the area in question, it is found that for mountainous regions of the globe, for which information is available so far, the geoid and topography go together.

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ON $\Gamma(k)$ IN WARING'S PROBLEM AND AN ANALOGOUS FUNCTION.

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1. Defining $\Gamma(k)$ as the least s such that every arithmetical progression contains an infinity of numbers which are sums of at most s positive kth powers, Hardy and Littlewood have shown that the upper limit of $\Gamma(k)$ is $4k$, while for 'almost all' k, $\Gamma(k) \leqslant k$.

Let us denote by $\Delta(k)$ the least s such that every arithmetical progression contains infinitely many numbers of the form $\pm x_1^k \pm \cdots \pm x_s^k$, where the x's are integers. Recently, Wright[1] has announced the following results:

THEOREM 1. $\Delta(\mathrm{k}) \leqslant \dfrac{3\mathrm{k}-1}{2}$ *for odd* k

THEOREM 2. $\Delta(\mathrm{k}) \leqslant 2\mathrm{k}$ *for even* k.

In this paper I have used an extension of a theorem of Davenport,[2] to give simple proofs of Theorems 1 and 2. In addition it is proved that

THEOREM 3. *Let* k *be a power of* 3, *then* $\Delta(\mathrm{k}) = \dfrac{3\mathrm{k}-1}{2}$.

THEOREM 4. *Let* k *be a power of* 2 *greater than* 2, *then* $\Delta(\mathrm{k}) = 2\mathrm{k}$.

THEOREM 5.[3] *Let* p_1 *and* p_2 *be different odd primes such that*

$$p_1 \not\equiv 1(p_2),\ p_2 \not\equiv 1(p_1).$$

Then

$$\Gamma(p_1^{m_1} p_2^{m_2}) \leqslant p_1^{m_1} p_2^{m_2} \qquad (m_1 > 0,\ m_2 > 0).$$

It is an immediate generalization of Theorem 5 that

THEOREM 6. *Let* $\mathrm{p}_1, \mathrm{p}_2, \cdots \mathrm{p}_r$ *be odd primes such that* $\mathrm{p}_i \not\equiv 1(\mathrm{p}_j)$ *where*

$$1 \leqslant i \leqslant r,\ 1 \leqslant j \leqslant r$$

Then

$$\Gamma(p_1^{m_1} p_2^{m_2} \cdots p_r^{m_r}) \leqslant p_1^{m_1} p_2^{m_2} \cdots p_r^{m_r}$$

where the m's *are integers* > 0.

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[1] *Quar. Jour. Math.* (Oxford Series), 1935, in a paper on Tarry's problem.

[2] *Journ. Lond. Math. Soc.*, 1935, **10**, 30-32.

[3] Theorems 5 and 6 are included in the result due to Hardy and Littlewood that $\Gamma(k) \leqslant k$ except for certain "exceptional cases"; our method is, however, different and much simpler. See their paper P. N. VIII, in *Proc. Lond. Math. Soc.*, 1928.

2. *Notation and Lemmas.*

$\Gamma(k, p^\theta)$ is conveniently defined as the least s such that every residue class (mod p^θ) is representable as $x_1^k + \cdots x_s^k$ where the x's are positive integers.

$\Delta(k, p^\theta)$ is defined analogously as the least s such that every residue class (mod p^θ) is representable as $\pm x_1^k \pm \cdots \pm x_s^k$ where the x's are integers.

We will denote by $\Gamma'(k, p^\theta)$, the least s such that every residue class (mod p^θ) is representable as $x_1^k + \cdots + x_s^k$ where the x's are integers $\geqslant 0$ and prime to p.

$\Delta'(k, p^\theta)$ will denote the least s such that every residue class (mod p^θ) is representable as $\pm x_1^k \pm \cdots \pm x_s^k$ where the x's are integers prime to p.

Primes $\geqslant 3$ are denoted by p, and $h = \phi(p^\theta)$ where ϕ is Euler's totient function.

Note that for odd k, $\Delta(k) = \Gamma(k)$ and that for all k, $\Gamma(k) \leqslant \Gamma'(k)$.

Lemma 1. *Let* $(k, p - 1) = 1$, *then*

$$x^k \equiv R \pmod{p}$$

is soluble provided $p \nmid R$.

Proof. Let g be a primitive root (mod p). The numbers

$$g^k, g^{2k}, \cdots, g^{(p-1)k} \tag{A}$$

are residues of kth powers and being mutually incongruent they are congruent (mod p) in some order to the numbers $1, 2, \cdots, p - 1$. Hence the lemma

Lemma 2. *The solubility of*

$$x^k \equiv R \pmod{p^\theta}$$

where $p \nmid k$, $p \nmid R$, *implies the solubility of*

$$x^k \equiv R \pmod{p^{\theta+1}}$$

Proof. Let $x^k = R + mp^\theta$; then

$$(x + m_1 p^\theta)^k = R + mp^\theta + kx^{k-1} m_1 p^\theta + M(p^{\theta+1})$$
$$= R + p^\theta (m + kx^{k-1} m_1) + M(p^{\theta+1})$$

Since $p \nmid k$, $p \nmid x$, we can choose m_1 to satisfy $m + m_1 kx^{k-1} \equiv 0 \pmod{p}$ and the lemma follows.

Lemma 3.[4] *Let* m *be any composite number and let* $\alpha_1, \cdots, \alpha_u$ *be* u *different residue classes* (mod m); *let* $\beta_1, \cdots, \beta_v$ *be* v *different residue classes*

[4] I have proved lemma 3 in a paper to appear shortly in the *Quar. Jour. Math.* As an application of this lemma I prove there that $\Gamma(k) \leqslant 4k$.

(mod m) *where one of the* β's *is* 0 *and the rest are prime to* m; *let* $\gamma_1, \cdots \gamma_w$ *be all those different residue classes representable as* $\alpha_i + \beta_j$ $(1 \leqslant i \leqslant u,\ 1 \leqslant j \leqslant v)$.

Then $w \geqslant u + v - 1$ *if* $u + v - 1 \leqslant m$ *and otherwise* $w = m$.

Lemma 4.[5] $\Gamma'(k, p^\theta) \leqslant \left[\dfrac{k}{1 - \frac{1}{p}}\right] + 1.$

Proof. Let g be a primitive root (mod p^θ). The kth powers

$$g^k,\ g^{2k},\ \cdots,\ g^{\left[\frac{h}{k}\right]k} \tag{B}$$

are mutually incongruent (mod p^θ) and prime to p. Consider the two cases:

(i) k/h. Applying lemma 3 s times to the numbers.

$$0,\ g^k,\ g^{2k},\ \cdots,\ g^{\frac{h}{k}\cdot k} \tag{C}$$

it is evident that $\Gamma'(k, p^\theta) \leqslant s$ if s is the least integer such that

$$s\left(\frac{h}{k} + 1\right) - (s - 1) \geqslant p^\theta$$

i.e.,

$$\text{if } s \geqslant \frac{p^\theta}{\frac{h}{k}} = \frac{k}{1 - \frac{1}{p}}.$$

which gives the desired result.

(ii) $k \nmid h$. Then it is easily seen that the set

$$0,\ g^k,\ \cdots,\ g^{\left[\frac{h}{k}\right]k},\ g^{\left(\left[\frac{h}{k}\right]+1\right)k} \tag{D}$$

consists of 0 and $\left[\dfrac{h}{k}\right] + 1 \left(> \dfrac{h}{k}\right)$ kth powers which are mutually incongruent (mod p^θ) and prime to p. The same argument as in (i) proves the lemma.

Lemma 5. *If* k *is odd* $\Gamma'(k, 2^\theta) \leqslant 2$.

Proof.

$$x^k \equiv R \pmod 2$$

is soluble if R is odd. Since k is odd it follows from lemma 2 that

$$x^k \equiv R \pmod{2^\theta} \qquad (\theta \geqslant 1)$$

is soluble for $2 \nmid R$ and since $2m + 2 = (2m + 1) + 1$ we require at most 2 kth powers, prime to 2, to represent every residue class (mod 2^θ).

Lemma 6. $\Gamma'(3, 3^\theta) = 4.$ $\qquad (\theta \geqslant 1)$

Proof. It is obvious from lemma 1 that $\Gamma'(3, 3) \leqslant 2$.

[5] $[y]$ denotes the greatest integer not exceeding y.

Let $\theta > 1$ and let g be a primitive root (mod 3^θ). The cubes $g^3, g^{2\cdot 3}, \cdots, g^{\frac{2\cdot 3^{\theta-1}}{3}\cdot 3}$ are mutually incongruent (mod 3^θ) and prime to 3, and hence there are at least $2\cdot 3^{\theta-2}$ cubic residues, incongruent (mod 3^θ) and prime to 3, which are necessarily $\equiv \pm 1$ (mod 9). Therefore *all* numbers $\equiv \pm 1$ (mod 9) are cubic residues (mod 3^θ). This shows that every residue class (mod 3^θ) requires at most 4 cubes prime to 3, and hence our lemma.

Lemma 7. $\Delta(3) = \Gamma(3) = 4$.

From lemma 5, $\Gamma(3, 2^\theta) \leqslant \Gamma'(3, 2^\theta) \leqslant 2$.

From lemma 4, $\Gamma(3, p^\theta) \leqslant \Gamma'(3, p^\theta) \leqslant [\frac{5\cdot 3}{4}] + 1$ for $p \geqslant 5$.

From lemma 6, $\Gamma(3, 3^\theta) \leqslant \Gamma'(3, 3^\theta) = 4$.

But $\Gamma(3) \leqslant \operatorname{Max}_q \Gamma(3, q^\theta)$

where q runs through all primes. Hence our result.

Lemma 8. *Let* k *be a power of* 3, *then*

$$\Delta(k) = \Gamma(k) = \frac{3k-1}{2}.$$

Proof. Let $k = 3^m$ ($m > 0$). The case $m = 1$ is proved in lemma 7. Let, therefore, $m \geqslant 2$. For $\theta \leqslant m$, it is obvious that $\Gamma(k, 3^\theta) \leqslant k$. Let $\theta \geqslant m + 1$ then the same type of argument as in lemma 6 shows that all numbers $\equiv \pm 1$ (mod 3^{m+1}) are cubic residues (mod 3^θ). The manner of the proof is now similar to that in lemmas 6 and 7. Lemma 8 is Theorem 3.

Lemma 9. $\Gamma'(\mathrm{k}, 3^\theta) \leqslant \dfrac{3\mathrm{k}-1}{2}$ *for odd* k.

Proof. Let $3 \nmid k$, then our result follows from lemmas 1 and 2. The case when k is a power of 3, follows from lemma 8.

Let $k = a3^m$, where $3 \nmid a$, $2 \nmid a$. Then $x^a \equiv \mathrm{R}$ (mod 3^θ) is soluble for $3 \nmid \mathrm{R}$ (lemmas 1 and 2). Hence $x^{a3^m} \equiv \mathrm{R}^{3^m}$ (mod 3^θ) is soluble for $3 \nmid \mathrm{R}$. It follows that

$$\Gamma'(a3^m, 3^\theta) = \Gamma'(k, 3^\theta) \leqslant \Gamma'(3^m, 3^\theta) = \frac{3\cdot 3^m - 1}{2} \leqslant \frac{3k-1}{2}$$

Proof of Theorem 1.

Let k be odd, then from lemma 5, $\Delta(k, 2^\theta) = \Gamma(k, 2^\theta) \leqslant \Gamma'(k, 2^\theta) \leqslant 2$.

From lemma 9, $\Delta(k, 3^\theta) = \Gamma(k, 3^\theta) \leqslant \Gamma'(k, 3^\theta) \leqslant \dfrac{3k-1}{2}$

and finally from lemma 4, $\Delta(k, p^\theta) = \Gamma(k, p^\theta) \leqslant \Gamma'(k, p^\theta) \leqslant \left[\dfrac{5k}{4}\right] + 1$ for $p \geqslant 5$.

Now $\Delta(k) \leqslant \underset{q}{\text{Max}}\ \Delta(k, q^\theta)$ where q runs through all primes and hence $\Delta(k) \leqslant \frac{3k-1}{2}$ for odd k.

Lemma 10. *Let* k *be a power of* 2, $\theta > 1$, $2 \nmid \mathrm{R}$; *then if* R *is a* k*th power residue* (mod 2^θ), $-\mathrm{R}$ *is not.*

Proof. We can find x such that

$$x^k \equiv \mathrm{R} \pmod{2^\theta} \tag{1}$$

Let it be possible to find y such that

$$y^k \equiv -\mathrm{R} \pmod{2^\theta} \tag{2}$$

Since $2 \nmid \mathrm{R}$ and therefore $2 \nmid y$, we can find z to satisfy

$$yz \equiv 1 \pmod{2^\theta}$$

From (2)

$$1 \equiv -\mathrm{R}z^k \pmod{2^\theta} \tag{3}$$

From (1) and (3)

$$(xz)^k \equiv -1 \pmod{2^\theta}$$

Since k is a power of 2 and $\theta \geqslant 2$ it would follow that -1 is a quadratic residue (mod 2^2), which we know to be false and hence the assumption of the solubility of (1) leads to a contradiction. Thus our lemma.

Lemma 11. $\Delta'(\mathrm{k}, 2^\theta) \leqslant 2\mathrm{k}$, *provided* k *is a power of* 2 *and* $\theta > 1$.

Proof. It is known that 5 belongs to the exponent $2^{\theta-2}$ (mod 2^θ). Let $h = \phi(2^\theta)$ then the set

$$0, 5^k, \cdots, 5^{\left[\frac{h}{2k}\right]k} \tag{E}$$

consists of 0 and $\left[\frac{h}{2k}\right]$ kth powers which are incongruent (mod 2^θ) and prime to 2. The kth powers

$$-5^k, -5^{2k}, \cdots, -5^{\left[\frac{h}{2k}\right]k} \tag{F}$$

are mutually incongruent (mod 2^θ), prime to 2, and it follows easily from lemma 10, that no member of (F) is congruent (mod 2^θ) to a member of (E).

(i) Let $2k/h$. Applying lemma 3 s times to the combination of the sets (E) and (F) it is evident that $\Delta'(k, 2^\theta) \leqslant s$ where s is the least integer such that

$$s\left\{2\left(\frac{h}{2k}\right)+1\right\} - (s-1) \geqslant 2^\theta$$

i.e., if $s \geqslant \frac{2^\theta}{\frac{h}{k}} = 2k$ and hence our lemma.

(ii) Let $2k \nmid h$. It is easy to see that the set

$$(G) \qquad 0, 5^k, \cdots, 5^{\left[\frac{h}{2k}\right]k}, 5^{\left(\left[\frac{h}{2k}\right]+1\right)k}, -5^k, \cdots, -5^{\left(\left[\frac{h}{2k}\right]+1\right)k}$$

consists of 0 and $2\left(\left[\frac{h}{2k}\right]+1\right) > \frac{2h}{2k} = \frac{h}{k}$ kth powers which are mutually incongruent (mod 2^θ) and prime to 2. Proceeding with the argument as in (i) we arrive at the desired result.

Lemma 12. *Let* k *be even and* $\theta > 1$, *then* $\Delta'(k, 2^\theta) \leqslant 2k$.

Proof. The case when k is a power of 2 is proved in lemma 11.

Let $k = a2^m$ where $2 \nmid a$. Then $x^a \equiv R \pmod{2^\theta}$ is soluble for $2 \nmid R$ (lemmas 1 and 2). Hence $x^{a2^m} \equiv R^{2^m} \pmod{2^\theta}$ is soluble for $2 \nmid R$. And therefore, using lemma 11

$$\Delta'(k, 2^\theta) \leqslant \Delta'(2^m, 2^\theta) \leqslant 2 \cdot 2^m \leqslant 2k.$$

Proof of Theorem 2.

Let k be even. It is obvious that $\Delta'(k, 2) \leqslant 2$.

For $\theta > 1$ it follows from lemma 12 that $\Delta'(k, 2^\theta) \leqslant 2k$ and finally, for $p \geqslant 3$, $\theta \geqslant 1$ it follows from lemma 4 that

$$\Delta'(k, p^\theta) \leqslant \Gamma'(k, p^\theta) \leqslant \left[\frac{3k}{2}\right] + 1 \leqslant 2k$$

and hence our theorem.

Proof of Theorem 4.

Let $k = 2^m$ ($m \geqslant 2$), then it is easily seen that 0 and 1 are the only kth power residues (mod 2^{m+2}). To represent 2^{m+1} (mod 2^{m+2}) we require exactly $2 \cdot 2^m$ kth powers, namely, $2 \cdot 2^m$ unities and hence $\Delta(k) = 2k$, when k is a power of 2 greater than 2.

Lemma 13. *Let* $2p \nmid k$, p/n, *then the congruence* $x^k + y^k \equiv n(p^\theta)$ *is soluble with* $xy \not\equiv 0 \pmod{p}$.

Proof. Since k is odd the congruence $x^k + y^k \equiv n \pmod{p}$ is soluble with $xy \not\equiv 0 \pmod{p}$. Lemma 13 now follows from lemma 2.

Lemma 14. *Let* $p \equiv 1 \pmod{k}$, $2 \nmid k$, *then* $\Gamma'(k, p^\theta) \leqslant k$ $(\theta \geqslant 1)$.

Proof. Let g be a primitive root of $p = bk + 1$. It is easily seen that the numbers ($b + 1$ in number)

$$(H) \qquad 0, g^k, g^{2k}, \cdots, g^{bk}$$

are mutually incongruent residues of kth powers. From lemma 3, applied s times to the set (H) it is evident that $\Gamma'(k, p) \leqslant s$ where s is the least integer such that

$$s(b+1) - (s-1) \geqslant bk + 1$$

i.e., if $s \geqslant k$.

Our lemma is proved for $\theta = 1$. For $\theta > 1$ the result follows with the help of lemmas 2 and 13.

In the following lemmas p_1 and p_2 will denote different odd primes such that

$$p_1 \not\equiv 1 \pmod{p_2}, \quad p_2 \not\equiv 1 \pmod{p_1}$$

Lemma 15. $\Gamma'(p_1^{m_1} p_2^{m_2}, p_1\theta) < p_1^{m_1} p_2^{m_2}$

Proof. Now,

$$x^{p_2^{m_2}} \equiv \mathrm{R}\ (p_1^{\theta})$$

is soluble for $p_1 \nmid \mathrm{R}$ (lemmas 1 and 2). Hence

$$x^{p_1^{m_1} p_2^{m_2}} \equiv \mathrm{R}^{p_1^{m_1}}\ (p_1\theta)$$

is soluble for $p_1 \nmid \mathrm{R}$. Therefore, using lemma 4,

$$\Gamma'(p_1^{m_1} p_2^{m_2}, p_1\theta) \leqslant \Gamma'(p_1^{m_1}, p_1\theta) \leqslant \frac{3p_1^{m_1}}{2} + 1 < p_1^{m_1} p_2^{m_2}.$$

Lemma 16. $\Gamma'(p_1^{m_1} p_2^{m_2}, p_2\theta) < p_1^{m_1} p_2^{m_2}$.

The proof is similar to that of the preceding lemma.

Lemma 17. *Let* p *be an odd prime such that*

$$p \neq p_1, p \neq p_2, p \not\equiv 1\ (p_1), p \not\equiv 1\ (p_2)\ ;\ \text{then}$$
$$\Gamma'(p_1^{m_1} p_2^{m_2}, p^{\theta}) \leqslant 2.$$

Proof. Lemmas 1 and 2.

Lemma 18. *Let* p *be an odd prime such that*

$$p \neq p_1, p \neq p_2, p \equiv 1\ (p_1), p \not\equiv 1\ (p_2)\ ;\ \text{then}$$
$$\Gamma'(p_1^{m} p_2^{m_2}, p^{\theta}) < p_1^{m_1} p_2^{m_2}.$$

Proof. Now,

$$x^{p_2^{m_2}} \equiv \mathrm{R}\ (p^{\theta})$$

is soluble for $p \nmid \mathrm{R}$ (lemmas 1 and 2). Hence

$$x^{p_1^{m_1} p_2^{m_2}} \equiv \mathrm{R}^{p_1^{m_1}}\ (p^{\theta})$$

is soluble with $p \nmid \mathrm{R}$. Therefore, using lemma 4

$$\Gamma'(p_1^{m_1} p_2^{m_2}, p^{\theta}) \leqslant \Gamma'(p_1^{m_1}, p^{\theta}) \leqslant \tfrac{3}{2} \cdot p_1^{m_1} + 1 < p_1^{m_1} p_2^{m_2}.$$

Lemma 19. *Let* p *be an odd prime such that*

$$p \neq p_1,\ p \neq p_2,\ p \not\equiv 1\ (p_1),\ p \equiv 1\ (p_2)\ ;\ \textit{then}$$
$$\Gamma'(p_1^{m_1}\ p_2^{m_2},\ p^\theta) < p_1^{m_1}\ p_2^{m_2}$$

Proof. The argument is similar to that in the preceding lemma.

Lemma 20. *Let* $p \equiv 1\ (p_1)$, $p \equiv 1\ (p_2)$; *then*

$$\Gamma'(p_1^{m_1}\ p_2^{m_2},\ p^\theta) \leqslant p_1^{m_1}\ p_2^{m_2}.$$

Proof. Since $p \equiv 1\ (p_1)$ and also $\equiv 1\ (p_2)$ it follows that $p \equiv 1\ (p_1\ p_2)$. Our lemma follows now from lemma 14.

Proof of Theorem 5.

From lemma 5 it is evident that

$$\Gamma(p_1^{m_1}\ p_2^{m_2},\ 2^\theta) \leqslant \Gamma'(p_1^{m_1}\ p_2^{m_2},\ 2^\theta) \leqslant 2.$$

Let $p > 2$, then it is evident from lemmas 14-20 that

$$\Gamma(p_1^{m_1}\ p_2^{m_2},\ p^\theta) \leqslant \Gamma'(p_1^{m_1}\ p_2^{m_2},\ p^\theta) \leqslant p_1^{m_1}\ p_2^{m_2}$$

and hence our theorem.

HETEROCYCLIC COMPOUNDS—PART I.

Coumarins from Cyclopentanone-2-Carboxylate and 4-Methylcyclopentanone-2-Carboxylate.

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SOME years ago, one of us (R.D.D.) published a paper on the synthesis of Coumarins from phenols and allylacetoacetic ester.[1] Owing to unavoidable circumstances, the work outlined therein could not be resumed. In the meanwhile, a considerable amount of work on the formation of coumarins and chromones from phenols and open-chain β-Ketonic esters has been published by D. Chakravarti and collaborators, and also by A. Robertson and co-workers.[2] A critical search of the literature revealed the presence of very little work on this type of condensation between phenols and cyclic β-Ketonic esters. Dieckmann[3] had studied the condensation of resorcinol and pyrogallol with 4-methylcyclopentanone-2-carboxylate and of resorcinol with cyclohexanone-2-carboxylate. The latter ester had also been condensed with *m*-cresol and α-naphthol by Sen and Basu[4] who had also studied the interaction of 5-methylcyclohexanone-2-carboxylate with phloroglucinol, orcinol and pyrogallol. This being the only work known, we thought it desirable to study the coumarin and chromone formations from the cyclic-β-Ketonic esters derived from cyclopentanone, alkylcyclopentanones, cyclohexanone, alkylcyclohexanones and *trans*-decalones, and the present paper describes our results of the formation of coumarins from the first two esters.

Phenol, *m*-creso *p*-cresol, resorcinol, 4-ethylresorcinol, 4 : 6-diethylresorcinol, orcinol, pyrogallol, phloroglucinol, α-naphthol, β-naphthol, guaiacol, *p*-nitrophenol, thymol and hydroquinone were condensed with cyclopentanone-2-carboxylate and 4-methylcyclopentanone-2-carboxylate in presence of either concentrated H_2SO_4 or phosphorous oxychloride as condensing agents. Resorcinol, 4-ethyl-resorcinol, α-naphthol and pyrogallol gave good yields of coumarins from both the Ketonic esters in presence of concentrated H_2SO_4; while phloroglucinol, orcinol and 4 : 6-diethylresorcinol condensed

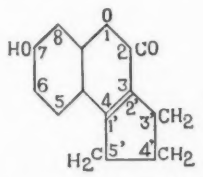
well in the presence of phosphorous oxychloride. The efficiency of this condensing agent in the case of open-chain β-Ketonic esters with polyhydride phenols had already been noted by one of us (Naik, Desai and Trivedi[5]). The yield of coumarins from cresols was not as good as that from the dihydric phenols, while phenol gave the poorest yield. β-Naphthol, guaiacol, *p*-nitrophenol, thymol and hydroquinone did not react in presence of concentrated H_2SO_4.

The coumarin structure was proved by their unusual stability to the hydrolytic action of caustic soda, when the original coumarins were always recovered. If they were the isomeric γ-pyrones, fission to *o*-hydroxycarboxylic acids or *o*-hydroxy-Ketones should have occurred. The stability of these types of coumarins had also been noticed by Sen and Basu (*loc. cit.*) in the case of cyclohexenocoumarines. These products are also insoluble in hydrochloric acid (1.1), and do not react with benzaldehyde in presence of sodium ethoxide. The isomeric γ-pyrones which we have prepared are soluble in hydrochloric acid, and form styryl derivatives (unpublished work).[6] Therefore, there is no doubt regarding the coumarin structure of the compound described in this communication. The coumarin from orcinol may have its hydroxyl group, either in the 5 or 7 position. Dey[7] has adopted the 5-hydroxy structure of the coumarin formed from orcinol and acetone dicarboxylic acid. As the behaviour of our coumarin from orcinol was similar to that of coumarins from 4 : 6-diethylresorcinol and phloroglucinol (*vide* experimental part), we are inclined to accept the 5-hydroxy structure for it.

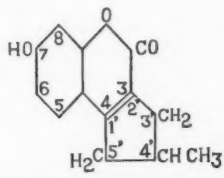
Sen and Chakravarti[8] were successful in mercurating coumarins from open-chain β-Ketonic esters ; while Naik and Patel[9] have studied the effect of substituents in the mercuration of these types of coumarins. As these interesting types of coumarins were in hand, we thought it interesting to mercurate them using the method of Sen and Chakravarti. The coumarins obtained from cyclopentanone-2-carboxylate, and 4-methylcyclopentanone-2-carboxylate with α-naphthol, pyrogallol, resorcinol, orcinol, phloroglucinol and 4-ethylresorcinol were mercurated giving similar types of results showing that the cyclopenteno- and methylcyclopenteno-rings in the 3 : 4-positions exerted similar influence. That some influence is exerted by the rings in 3 : 4-position is shown by the fact that different results are obtained by mercurating 3 : 4-cyclohexeno-coumarins (unpublished work). The coumarins from α-naphthol did not undergo mercuration, the reason being that the coumarin ring could not be opened up, while the coumarin from pyrogallol did not give a pure product. The coumarins from resorcinol, orcinol and phloroglucinol gave diacetoxymercuro-derivatives. The positions occupied

by acetoxymercuro groups are probably 6 and 8, because they are free in all these compounds, and the usual reactivity of coumarins is centred in these positions. The coumarin from 4-ethylresorcinol gave a mixture of mono and diacetoxy-mercuro-derivatives. This coumarin has its 6-position substituted by the ethyl group, and should have given only a mono-acetoxy-mercuro derivative, but our efforts to isolate it in a pure condition were unavailing. We are, however, examining the mercuration of coumarins obtained from 4-ethylresorcinol and open-chain β-Ketonic esters to clear up this point. The anomalous behaviour of coumarins with a negative substituent in 6-position has also been observed by Sen and Chakravarti[8] and Naik and Patel,[9] and our work supports other observations of these previous authors.

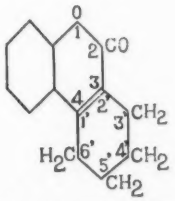
As we have studied the formation of coumarins from cyclic β-Ketonic esters having cyclopentane, cyclohexane and decalin rings, we wish to propose a nomenclature for them, as the one due to Dieckmann (*loc. cit.*) is not satisfactory. This is essentially based upon the nomenclature proposed for naphthacoumarins by Robinson and Rose.[10] These coumarins, as well as those which are to be described in the succeeding papers of this series, contain cyclopentene, cyclohexene and octalin rings fused to the coumarin ring in 3 : 4-positions, therefore, they should be called cyclopenteno-(1': 2': 4 : 3)-coumarin, cyclohexeno-(1': 2': 4 : 3)-coumarin and trans-octalino-(1 : 2 : 3 : 4)-coumarin. The numbering of the substituents in various rings could be illustrated by the following examples :—



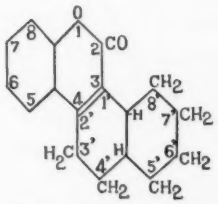
7-Hydroxy-cyclopenteno-(1': 2': 4 : 3)-coumarin



7-hydroxy-4'-methyl-cyclopenteno-(1': 2': 4 : 3) coumarin



Cyclohexeno-(1': 2': 4 : 3)-coumarin



Trans-octalino-(1': 2': 3 : 4)-coumarin

Experimental.

Cyclopentanone-2-carboxylate and 4-methylcyclopentanone-2-carboxylate were prepared by the method of Dieckmann.[3]

Cyclopenteno-(1': 2': 4 : 3)-*coumarin*.—To a mixture of phenol (6 g.) and cyclopentanone-2-carboxylate (9 g.), concentrated sulphuric acid (25 c.c., d. = 1·84) was slowly added with constant shaking and cooling. After allowing the mixture to stand at the room temperature for three days, it was poured on ice water, and the flocculent precipitate that separated out was collected, and crystallised from dilute alcohol (charcoal) when white needles, melting at 129°, were obtained (yield 0·5 g.). The sample dried in a vacuum over $CaCl_2$ was analysed. [Found: C, 74·4 ; H, 5·4 ; $C_{12}H_{10}O_2,\frac{1}{2}H_2O$ requires C = 73·8 ; H, 5·6 per cent.]

6-*Methylcyclopenteno*-(1': 2': 4 : 3)-*coumarin* was similarly prepared from para-cresol (5 g), the above ester (5 g.) and concentrated H_2SO_4 (20 c.c.). The solid (0·7 g.) crystallised from dilute alcohol in needles melting at 173°–174°. [Found : C, 77·6 ; H, 6·1 ; $C_{13}H_{12}O_2$ requires C, 78·0 ; H, 6·0 per cent.]

7-*Methylcyclopenteno*-(1': 2': 4 : 3)-*coumarin* was similarly prepared from *m*-cresol (5 g.), the above ester (5 g.) and concentrated H_2SO_4 (20 c.c.), and crystallised from dilute alcohol in needles (0·8 g) melting at 105°. [Found: C, 77·9 ; H, 6·3 ; $C_{13}H_{12}O_2$ requires C, 78·0 ; H, 6·0 per cent.] This, as well as the above two coumarins, did not dissolve in boiling caustic soda, and were recovered unchanged.

7-*Hydroxy-cyclopenteno*-(1': 2': 4 : 3)-*coumarin* was prepared from resorcinol (5 g.), the above ester (6 g.) and concentrated H_2SO_4 (20 c.c.), and crystallised from dilute alcohol in needles, m.p. 247° (yield 5·5 g.). [Found : C, 71·3 ; H, 5·1 ; $C_{12}H_{10}O_3$ requires C, 71·3 ; H, 5·0 per cent.] It dissolved in alkali with a blue fluorescence and was recovered unchanged after heating the solution for two hours.

The acetyl derivative prepared by heating the coumarin (0·5 g.) with acetic anhydride (5 c.c.) on a sand-bath for one hour crystallised from alcohol in glistening plates, m.p. 158–159.° [Found: C, 68·5 ; H, 5·1 ; $C_{14}H_{12}O_4$ requires C, 68·8 ; H, 4·9 per cent.]

The benzoyl derivative obtained by treating the pyridine solution of the coumarin (0·5 g.) with benzoyl chloride (1 c.c.) crystallised from dilute alcohol (charcoal) in needles, m.p. 166-167°. [Found : C, 74·5 ; H, 4·6 ; $C_{19}H_{14}O_4$ requires C, 74·8 ; H, 4·6 per cent.].

7-*Hydroxy*-6·8-*bis-acetoxy-mercuro-cyclopenteno*-(1' : 2' : 4 : 3)-*coumarin*.—The hydroxy-coumarin (1 g.) was dissolved in 5 per cent. caustic soda

(8 c.c.) and neutralised with 5 per cent. acetic acid (3·2 c.c.). This solution was then added to a solution of mercuric acetate (4 g. in 100 c.c. of water) gradually with vigorous shaking. The curdy precipitate was filtered off, washed with water under suction, dissolved in 2 per cent. sodium hydroxide solution, filtered, and reprecipitated with dilute acetic acid. The precipitate was again filtered, washed with water, and thoroughly extracted with boiling alcohol. A grey, amorphous powder which did not melt was finally obtained. [Found : Hg, 55·0 ; $C_{16}H_{14}O_7Hg_2$ requires Hg, 55·7 per cent.]

7-*Hydroxy*-6-*ethyl-cyclopenteno*-(1': 2': 4 : 3)-*coumarin* was prepared from 4-ethylresorcinol (6 g.), the ester (6 g.) and concentrated H_2SO_4 (30 c.c.), and crystallised from alcohol (charcoal) in colourless needles, m.p. 266°. [Found : C, 73·0 ; H, 5·8 ; $C_{14}H_{14}O_3$ requires C, 73·0 ; H, 6·1 per cent.] (Yield 3·2 g.)

The acetyl derivative was obtained by boiling the substance (1 g.) with acetic anhydride (10 c.c.) for four hours and crystallised from alcohol in needles, m.p. 168°. [Found : C, 70·5 ; H, 6·3 ; $C_{16}H_{16}O_4$ requires C, 70·6 ; H, 5·9 per cent.] It was mercurated under conditions used for the 7-hydroxy-coumarin, and purified as described before. The dried product gave 46·6 per cent. Hg. An equimolecular mixture of mono- and bis-acetoxymercuro-derivatives, *i.e.*, $\frac{1}{2}$ ($C_{16}H_{16}O_5Hg + C_{18}H_{18}O_7Hg_2$) requires Hg = 47·3 per cent.

5-*Hydroxy*-6 : 8-*diethyl-cyclopenteno*-(1': 2' : 4 : 3)-*coumarin*.—A mixture of the ester (1 g.), 4 : 6-diethylresorcinol (1 g.) and phosphorous oxychloride (4 c.c.) was warmed on a water-bath for about 5 to 10 minutes ; copious fumes of HCl were evolved, and the mixture after cooling was poured into water, warmed, and the precipitate filtered off. On crystallising from dilute alcohol (charcoal) colourless needles, m.p. 195°, were obtained (yield 0·6 g.). [Found : C, 74·4 ; H, 7·1 ; $C_{16}H_{18}O_3$ requires C, 74·4 ; H, 7·0 per cent.] The coumarin dissolved in dilute caustic soda with a yellow solution, which was non-fluorescent.

5-*Hydroxy*-7-*methyl-cyclopenteno*-(1': 2': 4 : 3)-*coumarin* was similarly prepared from the ester (3 g.), orcinol (2 g.) and phosphorous oxychloride (4 c.c.) and purified in an identical manner. When crystallised from methyl alcohol, colourless needles, m.p. 253–254°, were obtained (yield 2 g.). [Found : C, 71·8 ; H, 5·5 ; $C_{13}H_{12}O_3$ requires C, 72·2 ; H, 5·6 per cent.] It dissolved in alkali with a non-fluorescent yellow solution, and was recovered unchanged on acidification. *The acetyl derivative* prepared as usual crystallised from dilute alcohol in colourless needles, m.p. 139–140°. [Found : C, 69·4 ; H, 5·6 ; $C_{15}H_{14}O_4$ requires C, 69·7 ; H, 5·4 per cent.]

5-*Hydroxy*-7-*methyl*-6 : 8-*bis*-*acetoxymercuro*-*cyclopenteno*-(1': 2' : 4 : 3)-*coumarin* was prepared by the method used for the resorcinol analogue and was a grey, amorphous powder that did not melt. [Found : Hg, 53·8 ; $C_{17}H_{16}O_7Hg_2$ requires Hg, 54·6 per cent.]

5 : 7-*Dihydroxy*-*cyclopenteno*-(1': 2': 4 : 3)-*coumarin* was obtained from phloroglucinol (1·5 g.), the ester (2 g.) and phosphorous oxychloride (3 c.c.). After the usual purification, it crystallised from dilute alcohol in colourless needles, m.p. 273° (yield 1·5 g.). [Found : C, 63·1 ; H. 4·8 ; $C_{12}H_{10}O_4$, $\frac{1}{2}$ H_2O requires C, 63·4 ; H, 4·7 per cent.] Its alkaline solution was yellow and non-fluorescent.

The diacetyl derivative crystallised from dilute alcohol in colourless needless, m.p. 140°. [Found : C, 63·7 ; H, 4·8 ; $C_{16}H_{14}O_6$ requires C, 63·6; H, 4·7 per cent.]

5 : 7-*Dihydroxy*-6 : 8-*bis*-*acetoxy*-*mercuro*-*cyclopenteno*-(1': 2': 4 : 3)-*coumarin* was prepared by the usual method, and was an amorphous, grey powder that did not melt. [Found : Hg, 54·0 ; $C_{16}H_{14}O_8$ Hg_2 requires Hg, 54·5 per cent.]

7 : 8-*Dihydroxy*-*cyclopenteno*-(1': 2' : 4 : 3)-*coumarin* was prepared from the ester (3 g.), pyrogallol (2·5 g.) and phosphorous oxychloride (10 c.c.), and crystallised from methly alcohol (charcoal) in pinkish needles, m.p. 270° (yield 2 g.). [Found : C, 65·9 ; H, 4·2 ; $C_{12}H_{10}O_4$ requires 66·1 ; H, 4·4 per cent.] Its alkaline solution was reddish-yellow in colour, and did not fluoresce.

The diacetyl derivative crystallised from alcohol in colourless needles, m.p. 194°. [Found : C, 63·4 ; H, 4·7 ; $C_{16}H_{14}O_6$ requires C, 63·6 ; H, 4·7 per cent.]

Cyclopenteno-(1': 2': 4 : 3)-1 : 2-α-*naphthapyrone* was prepared from the ester (3 g.), α-naphthol (3 g.) and concentrated H_2SO_4 (15 c.c.). Crystallisation from alcohol gave pale-yellow needles, m.p. 218° (yield 3·5 g.). [Found : C, 81·1 ; H, 4·9 ; $C_{16}H_{12}O_2$ requires C, 81·3 ; H, 5·1 per cent.] The pyrone did not dissolve in dilute alkali, even on prolonged boiling.

Coumarins from 4-*methyl*-*cyclopentanone*-2-*carboxylate*.—This ester was condensed with the various phenols under conditions which were similar in all details to those adopted in the case of cyclopentanone-2-carboxylate. The yields of coumarins in the case of different phenols were also comparable. Therefore, only the necessary information is given in each case.

7-*Hydroxy*-4'-*methylcyclopenteno*-(1': 2': 4 : 3)-*coumarin* prepared from resorcinol crystallised from alcohol in colourless needles, m.p. 173°.

[Found: C, 72·0; H, 5·3; calc. for $C_{13}H_{12}O_3$; C, 72·2; H, 5·5 per cent.] Dieckmann (*loc. cit*) gives the m.p. 180°.

The acetyl derivative crystallised from alcohol in white, soft needles, m.p. 143–144° (Dieckmann gives 133–134°). [Found: C, 69·7; H, 5·4; calc. for $C_{15}H_{14}O_4$: C, 69·8; H, 5·4 per cent.]

7-*Hydroxy*-6 : 8-*bis-acetoxymercuro*-4'-*methylcyclopenteno*-(1' : 2': 4 : 3)-*coumarin* was a grey amorphous powder with no melting point. [Found: Hg, 53·2; $C_{17}H_{16}O_7Hg_2$ requires Hg, 54·6 per cent.]

6-*Ethyl*-7-*hydroxy*-4'-*methylcyclopenteno*-(1' : 2' : 4 : 3)-*coumarin* obtained from 4-ethyl-resorcinol crystallised from alcohol (charcoal) in colourless needles, m.p. 198°. [Found: C, 73·5; H, 6·6; $C_{15}H_{16}O_3$ requires C, 73·8; H, 6·6 per cent.]

The acetyl derivative crystallised from alcohol in colourless needles, m.p. 116°. [Found: C, 71·0; H, 6·2; $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3 per cent.]

Its mercuration gave an amorphous powder with no m.p. [Found: Hg, 46·6; $\frac{1}{2}(C_{17}H_{18}O_5Hg + C_{19}H_{20}O_7Hg_2)$ requires Hg, 46·3 per cent.]

5-*Hydroxy*-7-*methyl*-4'-*methylcyclopenteno*-(1': 2': 4 : 3)-*coumarin* prepared from orcinol crystallised from alcohol in colourless needles, m.p. 215–216°. [Found: C, 72·9; H, 6·3; $C_{14}H_{14}O_3$ requires C, 73·1; H, 6·1 per cent.] Its solution in dilute sodium hydroxide was deep-yellow and non-fluorescent.

The acetyl derivative crystallised from alcohol in needles, m.p. 107–108°. [Found: C, 70·5; H, 6·0; $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·8 per cent.]

The 6 : 8-*bis-acetoxymercuro-derivative* was an amorphous powder. [Found] Hg, 52·8; $C_{18}H_{18}O_7Hg_2$ requires Hg, 53·6 per cent.].

5-*Hydroxy*-6 : 8-*diethyl*-4'-*methylcyclopenteno*-(1': 2': 4 : 3)-*coumarin* prepared from 4 : 6-diethylresorcinol crystallised from dilute alcohol in needles, m.p. 181°–182°. [Found: C, 74·7; H, 7·6; $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·3 per cent.] Its alkaline solution was deep-yellow and non-fluorescent.

5 : 7-*Dihydroxy*-4'-*methylcyclopenteno*-(1': 2': 4 : 3)-*coumarin* prepared from phloroglucinol crystallised from dilute alcohol in needles or plates, m.p. 273°. [Found: C, 64·4; H, 5·3; $C_{13}H_{12}O_4$, $\frac{1}{2}H_2O$ requires C, 64·7; H, 5·4 per cent.]

The diacetyl derivative crystallised from alcohol in needles, m.p. 133–134°. [Found: C, 64·4; H, 5·0; $C_{17}H_{16}O_6$ requires C, 64·5; H, 5·1 per cent.]

The 6 : 8-*bis-acetoxymercuro-derivative* was a grey, amorphous powder. [Found: Hg, 53·4; $C_{17}H_{16}O_8Hg_2$ requires Hg, 53·4 per cent.]

4'-*Methylcyclopenteno*-(1': 2': 4 : 3)-1 : 2-α-*naphthapyrone* prepared from

α-naphthol crystallised from alcohol in needles, m.p. 167°. [Found: C, 81·8; H, 5·8; $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6 per cent.]

7 : 8-*Dihydroxy*-4'-*methylcyclopenteno*-(1': 2': 4 : 3)-*coumarin* obtained from pyrogallol crystallised from alcohol in needles, m.p. 240° (sintering at 230°). Dieckmann (*loc. cit.*) gives 207-210°. [Found : C, 67·4; H, 5·1; calc. $C_{13}H_{12}O_4$: C, 67·6; H, 5·3 per cent.]

The diacetyl derivative crystallised from methyl alcohol in needles, m.p. 118–119°. [Found: C, 64·4; H, 5·2; $C_{17}H_{16}O_6$ requires C, 64·6; H, 5·1 per cent.]

We have great pleasure in expressing our thanks to Dr. R. F. Hunter for his kind interest in this work, and to Dr. R. C. Shah for his helpful criticism and gift of 4-ethyl and 4 : 6-diethylresorcinols.

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THE RAMAN SPECTRA OF SOME SIMPLE MOLECULES.

(Dimethyl Ether, Phosgene, *n*-Butane, Ethylene Diamine, Ethylene Glycol, Ethylene Dichloride, Ethylene Dibromide, Acetylene Tetrachloride, Acetylene Tetrabromide and Hexachloroethane.)

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1. *Introduction.*

The results reported in the following pages are the outcome of a systematic study of the Raman spectra of certain relatively simple organic molecules which the author undertook some time back. Both from the theoretical as well as from the chemical standpoint, the importance of accurate data relating to the Raman spectra of such molecules, including the exact knowledge of the state of polarisation of the modified frequencies appearing in them, cannot be overemphasised. Although the vibrational Raman spectra of practically all the substances considered here have been repeatedly examined by previous investigators, polarisation data are lacking in many cases, where precisely such data appears to be of great importance. It was the desire to fill this existing gap that prompted the author to take up this investigation.

On the theoretical side, we are still not in a position to be able to compute the exact degree of depolarisation of a vibrational Raman line even in the case of very simple molecules. The polarisation rules enunciated by Placzek (1934) are based purely on the symmetry characters of the vibration concerned, and state that,

(i) the degree of depolarisation ρ of those Raman lines which arise from *totally symmetric* vibrations in zero in the case of molecules possessing cubic symmetry (*e.g.*, CH_4, SF_6, etc.), while for other molecules, ρ can take any value between 0 and $\frac{6}{7}$;

(ii) all the vibrational Raman lines which pertain to those fundamental vibrations of the molecule which are *not totally symmetric* will be depolarised ($\rho = \frac{6}{7}$);

(iii) *degenerate* vibrations are always depolarised.

We thus see that in so far as the assignment and classification of the Raman frequencies of a molecule are concerned,—barring those molecules which presumably possess cubic symmetry—it is generally more important to know whether they are polarised ($\rho < \frac{6}{7}$) or depolarised ($\rho = \frac{6}{7}$), rather than knowing the exact degree of depolarisation of the individual vibrational Raman lines. Indeed, the *exact* quantitative estimate of ρ involves extreme labour in the case of those molecules whose spectra comprise a large number of frequencies showing a wide range of intensities. The errors of photometry involved in the comparison of two lines of very different intensities are much more than those involved in the comparison of two lines of comparable intensities. For precisely the same reason, it is very often found (see Tables VI and VII) that while the quantitative estimate of the degree of depolarisation shows considerable discrepancies between different authors, the broad classification of the observed frequencies as polarised and depolarised, invariably shows very good agreement. In the present investigation, therefore, the author has followed the latter procedure, since it enables the study of a large number of substances without undue expense of time and labour. This was also the procedure adopted by the author (1936) in his investigations on the polarisation of the Raman lines of certain substances reported by him in previous papers wherein he pointed out remarkable regularities in the spectra of molecules such as $H \cdot C \cdot (CH_3)_3$, $N(CH_3)_3$, $H \cdot C \cdot Cl_3$, etc.

2. *Experimental.*

Dimethyl ether, phosgene and *n*-butane were condensed from commercial cylinders into thick-walled pyrex glass tubes of suitable size using a bath of alcohol and solid carbon dioxide; they were distilled several times in vacuum before sealing them off in the experimental tubes. The six ethane derivatives which are liquids at room temperature, and hexachloroethane which is a solid were Kahlbaum's purest chemicals. Ethylene dichloride, ethylene dibromide and acetylene tetrachloride were subjected to preliminary treatment in a fractionating column, and were subsequently distilled several times in vacuum into Wood tubes of pyrex glass (about 100 c.c. capacity) with flat end windows. Acetylene tetra-bromide was coloured light yellow, presumably due to dissolved bromine, but the distillate collected in vacuum by heating the surface of the liquid with a small flame was perfectly colourless. Glycol was distilled in a similar manner. In the case of ethylene diamine, only 5 grams of the substance were available, but there was no difficulty in photographing its spectrum.

The spectra of the liquids were photographed in the usual manner, partly on a Hilger two-prism spectrograph, and partly on a Fuess spectrograph

of larger dispersion. Hexachloroethane which is a solid at room temperature, was investigated by the technique of complementary filters. The duration of exposure varied very much from substance to substance, and was minimum in the case of the halogen derivatives of ethane which yielded very intense Raman spectra with an exposure of a few hours. In the case of $Br_2 \cdot HC \cdot CH \cdot Br_2$, the incident light was filtered by a saturated solution of $NaNO_2$, to prevent decomposition of the substance. In those cases where polarisation has been studied, the liquids were illumined by condensed light from a quartz mercury lamp, and the horizontal and vertical components of the transversely scattered radiation were photographed separately and simultaneously in the usual manner by the interposition of a double-image prism in the path of the scattered light.

3. *Results.*

In spite of repeated distillation, ethylene diamine and ethylene glycol were somewhat fluorescent; the spectra of the other substances, however, were absolutely free from background. The following tables give the Raman frequencies, with the estimated intensities (visual) and polarisation characters. In every case, results of recent investigations by other workers are also added for comparison.

P = polarised ($\rho \ll \frac{6}{7}$)

D = depolarised ($\rho \backsimeq \frac{6}{7}$)

PP – indicates a line which is highly polarised, the depolarisation factor being estimated to be generally less than 20 per cent.

TABLE I.

Dimethyl ether : $H_3C \cdot O \cdot CH_3$

Dadieu and Kohlrausch (1931)	Sirkar (1932)	Author
		160 ($\frac{1}{2}b$) P
	333 (0)	300 (0*bd*) P
	416 (0)	412 (1*b*) P
924 (2)	921 (2)	916 (*b*) P
	1102 (0)	1105 ?
(1150) (1)	..	*1155* ($\frac{1}{2}b$) D
1452 (1*vb*)	1454 (1*b*)	*1445* (6*vb*) D
2814 (5)	2814 (7)	2810 (10) P
(2862) (2)	2869 (3)	2863 (6) P
2914 (2)	2921 (3)	2916 (5) P
2953 (2)	2952 (3)	2951 (4) P
2990 (2)	2989 (3)	2986 (6) P

TABLE II.

Phosgene : $O = C\begin{matrix}Cl\\Cl\end{matrix}$

Dadieu & Kohlrausch	$\Delta\nu$	300	444	570	834	1810
	Int.	5	4	10	$\frac{1}{2}b$	4
Author	$\Delta\nu$	302	*442*	573	*832*	1807
	Int.	6	5	10	2*b*	5
	ρ	P	D	PP	D	P

TABLE III.

n-*Butane* : $H_3C \cdot H_2C \cdot CH_2 \cdot CH_3$.

Bhagavantam (1931)	Murray and Andrews (1933)	Kohlrausch and Köppl (1934)	Author
..	..	220 (0) ?	..
320 (0)	338 (0)	319 ($\frac{1}{2}$)	319 ($\frac{1}{2}$) P
430 (6)	428 (3)	426 (5)	430 (5) P
793 (4)	787 (2)	785 (2)	786 (3) P
834 (10)	832 (6)	838 (8)	828 (8) 837 (8) P
960 (3)	951 (1)	952 (1)	*953* (2*b*) D
983 (3)	980 (1)	978 (1)	979 (2*s*) P
1060 (6)	1058 (3)	1057 (4*b*)	1056 (4*s*) P
1067 (0)	1070 (0)	..	1070 (1*b*) P
1146 (4)	1149 (1)	1145 (2)	1144 (3*s*) P
1303 (3*b*)	1293 (1*b*)	1302 (2*b*)	*1302* (2*b*) D
1453 (4)	1450 (3*b*)	1450 (7*vb*)	*1445* (10*vb*) D
2665 (1)	2670 (0)	2663 ($\frac{1}{2}$)	2663 ($\frac{1}{2}$) P
2706 (1)	2702 (0)	2705 (2)	2701 (1) P
273 (2)	2739 (1)	2733 (5*b*)	2730 (4) P
2864 (4)	2864 (5)	2857 (10)	2858 (10) P
2879 (8)	2879 (10)	2875 (15)	2879 (15) P
2910 (3)	2912 (3)	2908 (8)	2910 (6*b*) P
2938 (6)	2949 (8)	2936 (15)	2940 (12) P
2964 (3)	2963 (3)	2966 (9)	*2967* (10) D ?

TABLE IV.

Ethylene diamine : $H_2N \cdot H_2C \cdot CH_2 \cdot NH_2$.

Kohlrausch and Köppl (1935)	Author	Kohlrausch and Köppl (1935)	Author
	186 ($\frac{1}{2}b$,	1346 (2)	1360 (2*b*)
322 (00)	333 ($\frac{1}{2}b$)	1452 (5*b*)	1445 (6*b*)
468 (2)	467 (3)		2661 ($\frac{1}{2}b$) ?
	510 (0)	2730 ($\frac{1}{2}$)	2743 (1*b*)
837 (3)	836 (5*b*)	2855 (7)	2848 (10*bd*)
	987 (0) ?	2891 (6)	2898 (8*b*)
	1051 (1*b*)	2928 (7*b*)	2932 (8*b*)
1092 (3*b*)	1093 (3)	3296 (7*b*)	3299 (8*b*)
	1240 (0)	3362 (5*b*)	3366 (6*b*)
1299 (2)	1296 (2)		

TABLE V.

Ethylene glycol : $HO \cdot H_2C \cdot CH_2 \cdot OH$.

Kohlrausch and Köppl (1935)	Author	Kohlrausch and Köppl (1935)	Author
342 (00)	340 (1*b*) P	..	1227 ($\frac{1}{2}b$) ?
478 ($\frac{1}{2}$)	475 (2) P	1258 (1)	*1260* (3*b*) D
512 (00)	*520* (1) D	1457 (4*b*)	*1450* (8*b*) D
862 (5*b*)	865 (8) P	2709 ($\frac{1}{2}$)	2712 (1*b*) P
	900 (1) D	2866 (7*vb*)	2860 (10*b*) P
1033 (1)	*1035* (2*b*) D	2926 (8*vb*)	2945 (10*vb*) P
1059 (1)	*1060* (2*b*) D ?		~3400 (2*vb*) P
1086 (2*b*)	1090 (4) P		O–H band width ~ 300 cm.$^{-1}$

TABLE VI.

Ethylene dichloride : $Cl \cdot H_2C \cdot CH_2 \cdot Cl$.

Trumpy (1935)		Kohlrausch and Ypsilanti (1935)	Cheng (1935)		Mizushima, Morino and Noziri (1936)	Author	
$\Delta\nu$	ρ	$\Delta\nu$	$\Delta\nu$	ρ	$\Delta\nu$	$\Delta\nu$	ρ
		125 (3)			124(2*b*)	*123* (4*b*)	D
260 ($\frac{1}{2}$)	P ?	265 (2)	264 (1)	0·52	265 (1)	263 (2)	P
300 (5)	0·3	301 (7)	298 (5*b*)	0·3	301 (5)	302 (8)	P
410 (1)	0·87	410 (3)	*410* (1)	0·91	412 (2)	*411* (3)	D
651 (10)	0·18	652 (9)	653 (5)	0·16	652 (8)	654 (10)	PP
672 (1)	0·88	675 (4)	*676* (2)	D ?	676 (2)	*675* (3)	D
754 (12)	0·26	751 (12)	749 (12*b*)	0·41	753 (10*b*)	754 (15*b*)	P
880 (0)	D	875 (1)	879 (1)	0·76	878 (1)	*880* (1)	D
940 (3)	0·5	942 (2)	940 (1)	0·17	941 (2)	940 (2)	P
			990 (0)	—			
			1022 ($\frac{1}{2}$)	0·83			
		1048 (2)	1047 (1)	0·55	1050 (0)	1052 (1)	P
		1143 ($\frac{1}{2}$)	*1141* ($\frac{1}{2}$)	0·89	1145 (1)	*1144* ($\frac{1}{2}$)	D
		1205 (2)	1204 (1)	0·36	1206 (0)	*1206* (2)	D
		1260 (2)	1264 (0)	—	1263 (1)	*1262* (1)	D
		1303 (4)	1300 (3)	0·29	1303 (3)	1302 (3)	P
		1429 (4*b*)	*1433* (2*b*)	0·8	1428 (3)	*1429* (3)	D
1440 (36)	0·83					*1440* ($\frac{1}{2}$)	D
						2844 (1)	?
		2871 (1)			2872 (0)	2872 (1)	P
2953 (15)	0·15	2956 (10)	2953 (8)	0·08	2955 (8)	2956 (12*b*)	PP
3000 (3)	0·85	3001 (5)	*2998* ($\frac{1}{2}$)	D	2999 (4*b*)	*3002* (4*b*)	D

TABLE VII.

Ethylene dibromide: $Br \cdot H_2C \cdot CH_2 \cdot Br$.

Trumpy (1935)		Kohlrausch and Yp- lanti (1935)	Cheng (1935)		Mizushima, Merino & Noziri (1936)	Author	
$\Delta\nu$	ρ	$\Delta\nu$	$\Delta\nu$	ρ	$\Delta\nu$	$\Delta\nu$	ρ
		90 (2)			90 (0*b*)	*92* (2*b*)	D
189 (8)	0·29	190 (12)	187 (10*b*)	0·5	189 (9)	189 (10)	P
		245 (1)	235 ($\frac{1}{2}$)	0·55	232 (0*b*)	228 (1*b*)	P
						320 (0)	?
		358 (3)	*356* (1)	0·86	356 (1)	*358* (2)	D
						470 (0)	?
554 (3)	0·07	557 (8)	552 (5)	0·19	552 (5)	551 (8)	PP
		589 (4)	*583* (2)	D ?	586 (2*b*)	*580* (2*b*)	D
657 (20)	0·33	660 (15*b*)	658 (15*b*)	0·43	660 (10*b*)	659 (15*b*)	P
						790 (0)	?
		843 (0)				*834* ($\frac{1}{2}$)	D
		904 (1)	897 (1)	0·44	897 (0)	895 (1)	P
			934 ($\frac{1}{2}$)	0·5	930 (0*b*)	930 (1*b*)	P?
1048 (2)	D ?	1057 (5)	*1047* (4)	0·85	1053 (4)	*1051* (6)	D
		1108 (0)	*1098* ($\frac{1}{2}$)	0·89	1091 (0)	1086	? ?
		1178 ($\frac{1}{2}$)	1165 (0)	—		*1169* ($\frac{1}{2}$)	D
						1187 (0)	D
1252 (9)	0·38	1255 (10)	1251 (10*b*)	0·59	1254 (6)	1256 (10*b*)	P
					1276 (1)	1295 (1*s*)	P
		1421 (2)	1419 ($\frac{1}{2}$)	0·75	1418 (1)	*1419* (1)	D
1440 (2)	0·7	1440 (3)	*1434* (2*b*)	0·86	1440 (2*b*)	*1436* (2)	D
		2864 (1)				2852 (1)	PP
2950 (8)	0·15	2954 (5)	2950 (2)	0·22	2953 (3)	2950 (6)	PP
2968 (8)	D	2969 (8)	2965 (8*b*)	0·08	2971 (5)	2970 (8)	PP
		3013 (2)	*3012* (1)	D	3013 (2)	*3012* (2*b*)	D
		3041 (2)	*3039* (1)	D			

TABLE VIII.

Acetylene tetrachloride : $Cl_2 \cdot HC \cdot CH \cdot Cl_2$

Trumpy (1935)		Kohlrausch and Ypsilanti (1935)	Mizushima, Morino and Noziri (1936)	Author
$\Delta\nu$	ρ	$\Delta\nu$	$\Delta\nu$	$\Delta\nu$
		89 (10*b*)	91 (10*b*)	92 (8*b*)
171 (5)	0·62	178 (7)	179 (6)	173 (6*b*)
		224 (2)	226 (2)	222 (2)
238 (4)	0·60	239 (7)	243 (6)	242 (6*s*)
289 (4)	D ?	290 (8)	289 (7)	289 (7*s*)
		324 (1)	327 (0)	324 (00*d*) ? ?
350 (8)	0·14	354 (8) (doublet)	353 (8)	353 (10)
			364 (3)	366 (7*s*)
		400 (3)	402 (0)	(400) (00) ? ?
540 (2)	D	544 (6)	547 (4)	544 (6)
641 (6)	0·05	647 (11)	650 (10)	647 (10)
		758 (5)	764 (3)	764 (5)
799 (7*b*)	0·51	795 (12)	802 (11)	799 (10*b*)
		1017 (3)	1016 (1)	1013 (1)
1210 (1)	D	1214 (4)	1218 (3)	1219 (3)
		1242 (1)	1242 (1)	1240 (1)
		1276 ($\frac{1}{2}$)	1280 (1)	1280 (1)
		1303 ($\frac{1}{2}$)	1306 (1)	1310 (1)
2980 (9)	0·3	2982 (8*b*)	2986 (10)	2986 (10)

TABLE IX.

Acetylene tetrabromide : $Br_2 \cdot HC \cdot CH \cdot Br_2$.

Trumpy (1936)	Gockel (1935)	Author	Trumpy (1936)	Gockel (1935)	Author
	61 (2)	*61* (6*b*) D			740 (0) P
	115 (5)	*113* (4) D ?			*800* (0) D
147 (0) P	148 (5)	148 (4*s*) P		1012 (1)	1012 (3) PP
175 (2) 0·86	181 (6)	*176* (5) D		1035 (0)	1030 (1) P
		184 (1) D	1140 (1) P ?	1139 (0)	*1133* (1) D
		197 ($\frac{1}{2}$) D		1150 (2)	*1151* (2) D
220 (4) 0·15	220 (8)	219 (10*s*) PP		1198 (4)	1196 (4*s*) P
		242 (1*s*) PP		1236 (0)	1222 ($\frac{1}{2}$) P
450 (1) D	452 (4)	*449* (4) D			*1250* ($\frac{1}{2}d$) D
532 (3) 0·09	538 (6)	537 (8) PP		1282 ($\frac{1}{2}$)	1281 (1) P
665 (1) P	665 (4)	664 (4) PP			1405 ($\frac{1}{2}d$) P
707 (6) 0·68	713 (8)	713 (15*b*) P	2985 (3) 0·37	2981 (4*b*)	2986 (4) P

TABLE X.

Hexachloroethane : $Cl_3C \cdot Cl_3$.

Mizushima and Morino (1936)	$\Delta\nu$	223	336	430	853	..
	Int.	5	5	8	5	
Author	$\Delta\nu$	220	344	431	852	980
	Int.	2	3	8*s*	5*b*	2

4. *Discussion of Results.*

(1) *Dimethyl ether*: $H_3C \cdot O \cdot CH_3$.—From the study of electron diffraction in the vapour of di-methyl ether, Sutton and Brockway (1935) determined the following constants for the molecule of this substance :

angle $C\hat{O}C = 110° \pm 4°$.

$$d_{c-o} = 1 \cdot 44 \pm \cdot 03 \text{ A} ; \; d_{c-c} = 2 \cdot 39 \pm \cdot 05 \text{ Å}.$$

If we regard the CH_3 groups as units, the molecule of dimethyl ether has the symmetry C_{2v} of the bent AB_2 molecule (*e.g.*, SO_2). Of the three fundamental frequencies of such a molecule, two are totally symmetric ($\rho < \frac{6}{7}$) and the third one anti-symmetric ($\rho = \frac{6}{7}$). Polarisation results enable us to identify the three frequencies. Employing Mecke's rotation, we have

$$\omega_1 = \nu(\sigma) = 1155 ; \; \omega_2 = \nu(\pi) = 916 ; \; \omega_3 = \delta(\pi) = 412.$$

From these three frequencies determined spectroscopically, and the molecular constants determined by electron diffraction, it is possible to make a rough computation of the C—O and C—C force constants.

(2) *Phosgene*, $O = C\begin{matrix} Cl \\ \diagup \\ \diagdown \\ Cl \end{matrix}$.—Brockway, Beach and Pauling (1935) found from the study of electron diffraction that the molecule of phosgene has got a planar configuration with the symmetry C_{2v}, and the molecular constants $d_{c-o} = 1 \cdot 28 \pm \cdot 02$ Å, $d_{c-cl} = 1 \cdot 68 \pm \cdot 02$ Å and angle $Cl\hat{C}Cl = 117° \pm 2°$. Henri and Howell (1930) made an elaborate study of the ultra-violet absorption spectrum of phosgene vapour. Kohlrausch and Pongratz (1934) have discussed the vibrational Raman spectrum of this substance and have given the following diagrammatic representation of the normal modes of vibration.

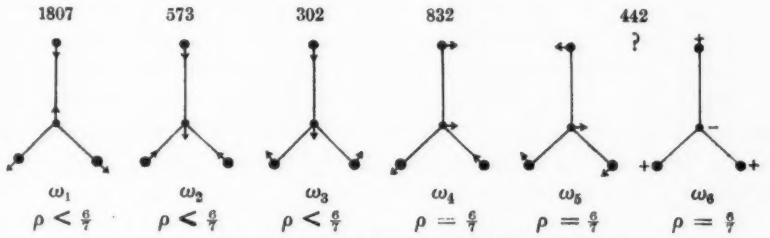

FIG. 1. Normal modes of vibration of the phosgene molecule.

There are six distinct vibrations all of which are allowed in the Raman effect as well as in the infra-red. ω_1, ω_2 and ω_3 are totally symmetric, and hence should be polarised in the Raman effect ; ω_4, ω_5 and the perpendicular vibration ω_6 should be depolarised. The Raman spectrum of phosgene, however,

shows only five characteristic frequencies. Kohlrausch and Pongratz have given a tentative classification of these frequencies which requires modification in view of the author's polarisation measurements. Of the three totally symmetric vibrations, ω_1, ω_2 and ω_3, we see that ω_1 and ω_2 are primarily valence oscillations, while ω_3 is a deformation oscillation. Polarisation measurements enable us to identify these three frequencies as,

$$\omega_1 = 1807\ ;\ \omega_2 = 573\ ;\ \omega_3 = 302.$$

Of the other three vibrations, ω_4 is of the valence type and hence can be identified with the Raman line at 832 cm.$^{-1}$ ω_5 and ω_6 are deformation oscillations; a unique assignment of the depolarised frequency 442 cm.$^{-1}$ to one or other of these two vibrational modes is not possible.

The Ethane derivatives, $X \cdot H_2C \cdot CH_2 \cdot X$ and $X_2 \cdot HC \cdot CH \cdot X_2$.—The Raman spectra of the ethane derivatives are of great interest because classical organic chemistry postulates the existence of "free rotation" about the C—C bond in the case of such compounds. Chemical evidence in support of the postulate of "free rotation" is, however, only of an indirect nature since it depends upon the non-existence—from the chemical standpoint—of stereo-isomeric compounds of the type $X_2 \cdot HC \cdot CH \cdot X_2$, $X \cdot H_2C \cdot CH_2 \cdot X$, etc. Of course, this does not preclude the possibility that such isomers do exist, if the chemical methods are incapable of isolating them in the free state. During the last few years, the application of physical and mathematical methods to the problem has made it clear that "free rotation" in the sense postulated by classical organic chemistry does not exist, and can at best be only a limiting case of very high temperatures. Theoretical investigation of the intra-molecular potential of ethane and its symmetrically substituted derivatives has shown that the *trans*-configuration has the minimum potential energy, while the *cis*-configuration corresponds to a maximum in the potential energy curve plotted as a function of the azimuth of the two rotating groups. This means that the *trans*-configuration is the most stable one, while the *cis*-configuration is the least stable. Between these two extreme limits, there are, in general, other configurations for which the potential energy curve exhibits minima of a more, or less pronounced character depending upon the nature of the substituents.

Study of electron diffraction by Wierl (1932), and of X-ray diffraction by Ehrhardt (1932) in the vapours of ethylene dichloride and ethylene dibromide, made it clear that the *trans*-configuration alone could not explain the observed results. Mizushima, Morino and Higasi (1934) made an elaborate study of the variation of the dipole moment of these two substances with temperature in different solvents. They found a systematic increase

of the dipole moment with temperature in the case of the chloride as well as of the bromide. Since the *trans*-configuration has no dipole moment, while a departure from this configuration gives rise to a finite dipole moment, these authors explained their results by postulating hindered rotation of the two groups about the *trans*-configuration, the amplitude of the oscillatory rotation increasing with temperature. This postulate had also been found to be sufficient to explain the results of X-ray and electron diffraction.

Kohlrausch (1932) was the first to draw attention to the importance of the study of the Raman spectra of the ethane derivatives from the standpoint of the problem of free rotation. In a series of papers published during the last two years, Kohlrausch and his collaborators (1935) on the one hand and Mizushima, Morino and co-workers (1935-36) on the other have discussed the Raman spectra of ethane derivatives in relation to the problem of free rotation. Unfortunately, their view-points are rather conflicting, and indeed do not admit of reconciliation. While Mizushima and Morino definitely eschew the *cis*-configuration because theoretically it is the least stable, Kohlrausch appears to be of opinion that it is necessary to postulate the co-existence of the *cis*- and *trans*-types of molecules to explain the spectra of ethane derivatives of the type $X \cdot H_2C \cdot CH_2 \cdot X$ where $X = CH_3$, Cl, Br, etc.

The theoretical discussion of the vibrations of a molecule of this type is considerably simplified if we treat it as a four-body problem, considering X and CH_2 as units. In such a case, the *trans*- and *cis*-configurations of the molecule will have all the four units in the same plane, and are represented diagrammatically by Fig. 2 *a* and Fig. 2 *b* respectively. The *trans*-configuration

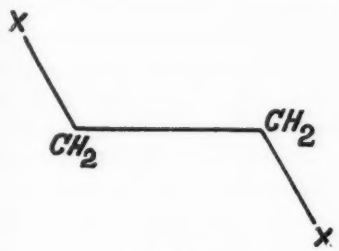

FIG. 2 *a*

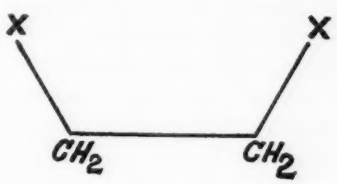

FIG. 2 *b*

has a centre of symmetry, and hence according to Placzek's selection rules, all those vibrations which are anti-symmetric to the centre of symmetry—this is one-half the total number—are forbidden in the Raman effect. The *cis*-form on the other hand does not possess a centre of symmetry, and so all the vibrations are allowed in the Raman effect; one-half of this total

number will be depolarised. Thus in the simple case of the four-body problem, the *trans*-form of the molecule ought to show three Raman lines all of which are polarised, while the *cis*-form should give rise to six Raman lines of which three are depolarised.

According to Kohlrausch, all frequencies less than 1000 cm.$^{-1}$ in the spectra of the 1, 2 di-halogen derivatives of ethane can be regarded as the chain frequencies, *i.e.*, frequencies pertaining primarily to the four-body configuration X·C·C·X. In this frequency interval, the dichloro and dibromo ethanes show at least nine frequencies. A single molecular configuration alone cannot explain this total number of observed frequencies. We also see that some of these frequencies are depolarised. This indicates the presence of symmetry in the molecule, which is possible only if all the four units lie in the same plane. The total number of observed frequencies as well as their polarisation characters are intelligible in a general manner, if one postulates the co-existence of the *cis*- and *trans*-configurations.

The above arguments are of a very general nature. Kohlrausch and Ypsilanti (1935) have also proposed a classification of the frequencies below 1000 cm.$^{-1}$ in the case of the molecules $Cl \cdot H_2C \cdot CH_2 \cdot Cl$, $Br \cdot H_2C \cdot CH_2 \cdot Br$, $H_3C \cdot H_2C \cdot CH_2 \cdot CH_3$, etc., between the various vibrational modes of the probable *cis*- and *trans*-forms of such molecules. However, as they have remarked, the assignment proposed by them is not free from difficulties. It might be mentioned here that the identification of the Raman frequencies 92 cm.$^{-1}$ of $Br \cdot H_2C \cdot CH_2 \cdot Br$ and 263 cm.$^{-1}$ of $Cl \cdot H_2C \cdot CH_2 \cdot Cl$, to similar vibrational modes of these molecules, is inconsistent with the observed states of polarisation of these two lines, because, the latter is polarised while the former appears to be depolarised. From the present investigation, we also notice the significant fact that the number of depolarised frequencies in the case of *n*-butane is much less than in the case of the corresponding dihalogen compounds. While the entire butane spectrum shows only three or perhaps four depolarised frequencies, we see as many as ten depolarised Raman lines in the spectra of 1, 2 dichloro and dibromo ethanes.

Mizushima and Morino have pointed out that certain frequencies attributed by Kohlrausch to the *cis*-configuration of the molecules of ethylene dichloride and ethylene dibromide can be regarded as the anti-symmetric vibrations of the *trans*-configuration which, though normally forbidden in the Raman effect, appear in the spectra of these compounds because of the hindered rotation of the two groups about the *trans*-position. The symmetry of the *trans*-form of the molecule is virtually obliterated by such rotation so that all the vibrations of the *trans*-configuration are rendered

Raman-active. In support of this view, they adduce the experimental fact observed by them that such lines are absent in the Raman spectra of the solid ethylene dihalides, wherein, presumably all the molecules exist only in the *trans*-state, and hindered rotation about this configuration is inhibited.

However, as far as the present author can see, Mizushima, Morino and others have not accounted for the existence of the depolarised frequencies in the spectra of the liquid ethylene dihalides, on which Kohlrausch has based some of his main arguments. In later communications, they have also expressed the view that probably discrete rotational isomers are present in the liquid state. Although, the remarkable differences between the spectra of the solid and liquid ethylene dihalides discovered by them are very significant, it is necessary to make sure that the spectra of the solids reported by them are complete. Indeed, in the case of solid hexachloroethane, the frequency 980 cm.$^{-1}$ is very clearly recorded in the spectrum of the solid photographed by the technique of complementary filters, while Mizushima and Morino failed to notice its presence in the solid spectrum.

The discussion of the spectra of acetylene tetrachloride and tetrabromide is more difficult, and is not possible at this stage. The author hopes to return to these questions on a future occasion.

In conclusion, the author's grateful thanks are due to Professor Sir C. V. Raman for his kind interest in the present work.

Summary.

The Raman spectra of dimethyl ether, phosgene, *n*-butane, ethylene diamine, ethylene glycol, ethylene dichloride, ethylene dibromide, acetylene tetrachloride, acetylene tetrabromide and hexachloroethane have been studied afresh. The Raman frequencies of phosgene have been classified with the aid of polarisation data. Polarisation measurements have also been made in the case of *n*-butane, ethylene glycol, ethylene dichloride, ethylene dibromide, and acetylene tetrabromide. A brief discussion of the spectra of the ethane derivatives in relation to the problem of "free rotation" is added.

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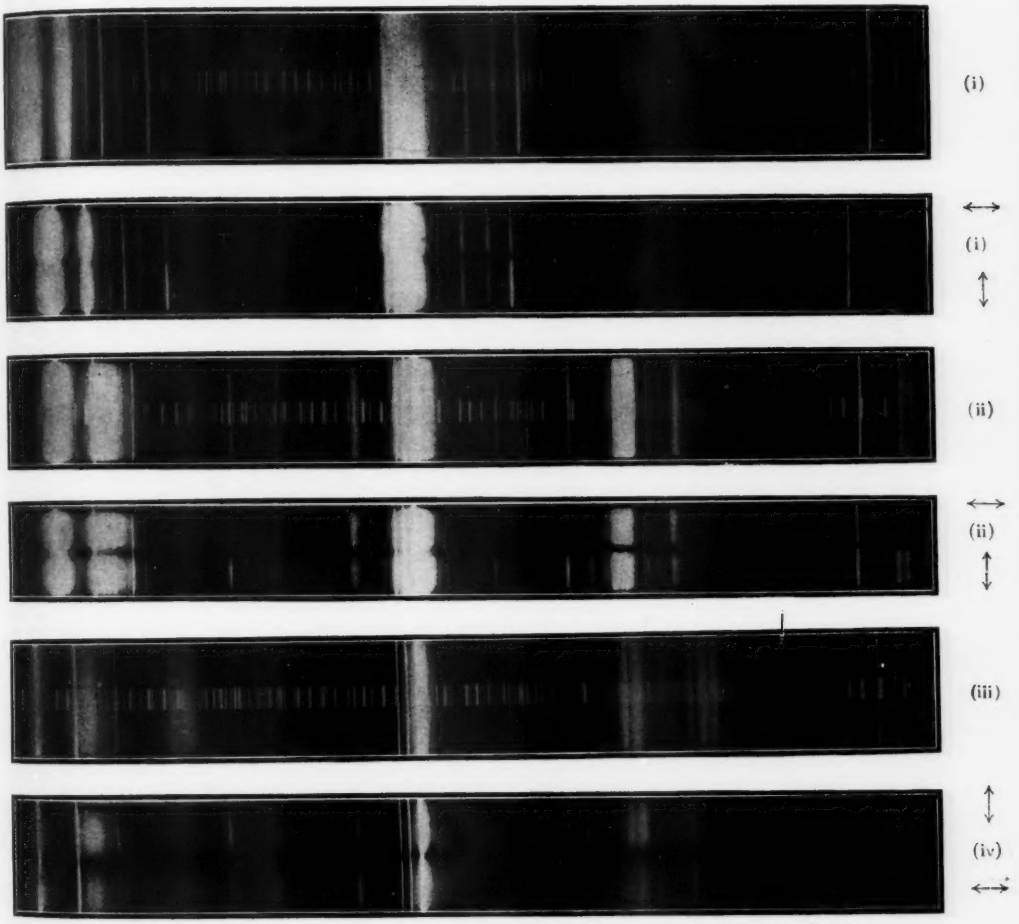

FIG. 3. Raman Spectra of

(i) $O{=}C{<}^{Cl}_{Cl}$; (ii) $H_3C{\cdot}H_2C{\cdot}CH_2{\cdot}CH_3$; (iii) $H_2N{\cdot}H_2C{\cdot}CH_2{\cdot}NH_2$; (iv) $HO{\cdot}H_2C{\cdot}CH_2{\cdot}OH$

λ4046
λ4046

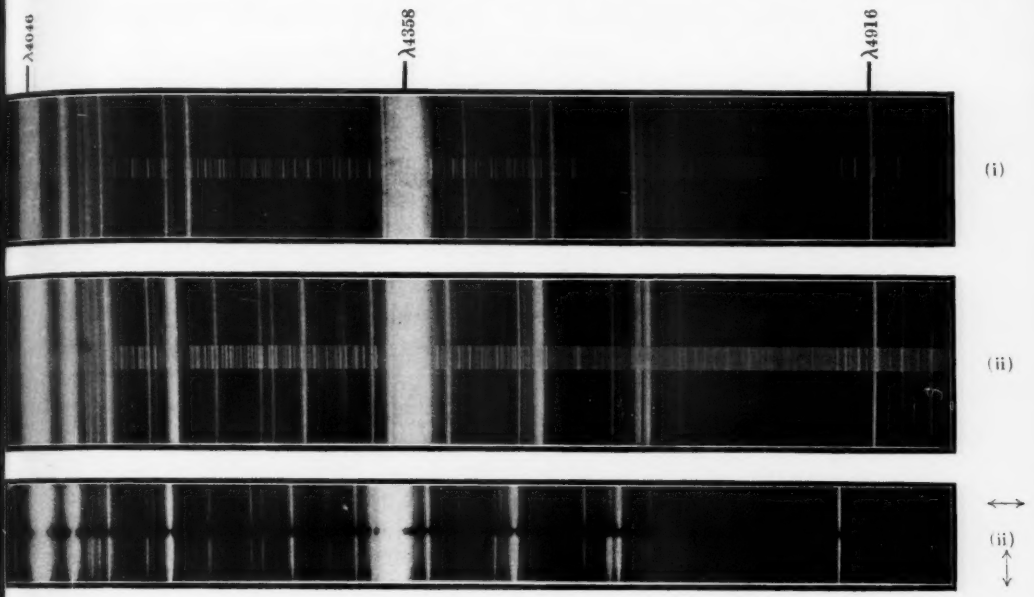

FIG. 4. Raman Spectra of
(i) $Cl \cdot H_2C \cdot CH_2 \cdot Cl$; (ii) $Br \cdot H_2C \cdot CH_2 \cdot Br$

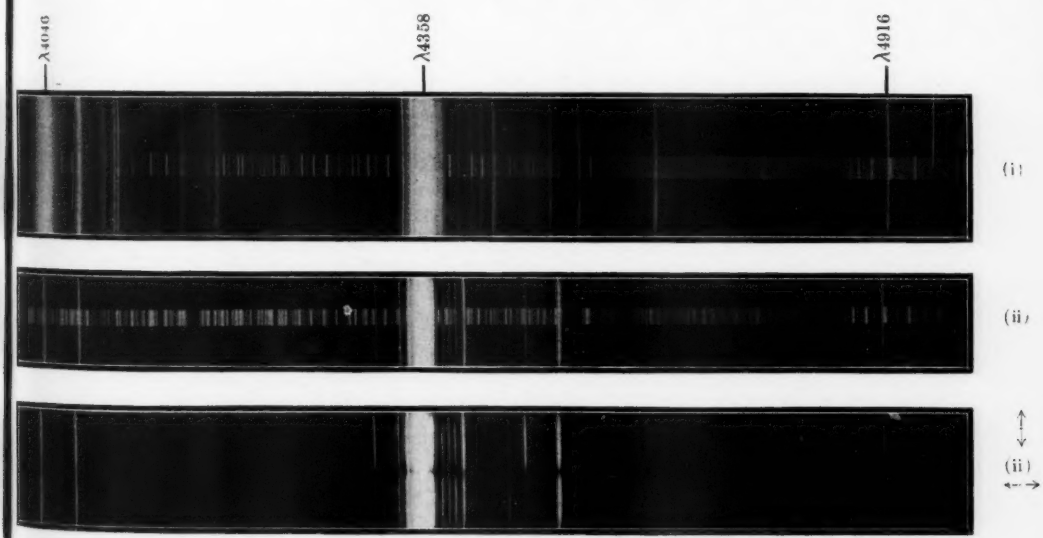

FIG. 5. Raman Spectra of
(i) $Cl_2 \cdot HC \cdot CH \cdot Cl_2$; (ii) $Br_2 \cdot HC \cdot CH \cdot Br_2$

MICROPHONE ACTUATED THYRATRON RELAY.

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In recent years the gaseous triodes and particularly the mercury vapour type generally known as the thyratrons are finding extensive applications in science and industry and quite a number of papers have been published on the properties and varied uses of these tubes. One of the important and wide application of the tube is as a sensitive relay which can be actuated by a very small input power at the grid. The input required at the grid to actuate the relay is so extremely small that it can be operated directly by a photoelectric cell or by the ionization current due to a cosmic particle. However it does not seem to have received much attention that the relay may be actuated by a microphone directly coupled to the grid and such a simple device may find many applications in acoustics. Experiments conducted in this laboratory gave interesting results and showed that the relay could be used in quantitative experiments as well. The present paper is concerned with the simple microphone operated thyratron relay and some of its applications in acoustics.

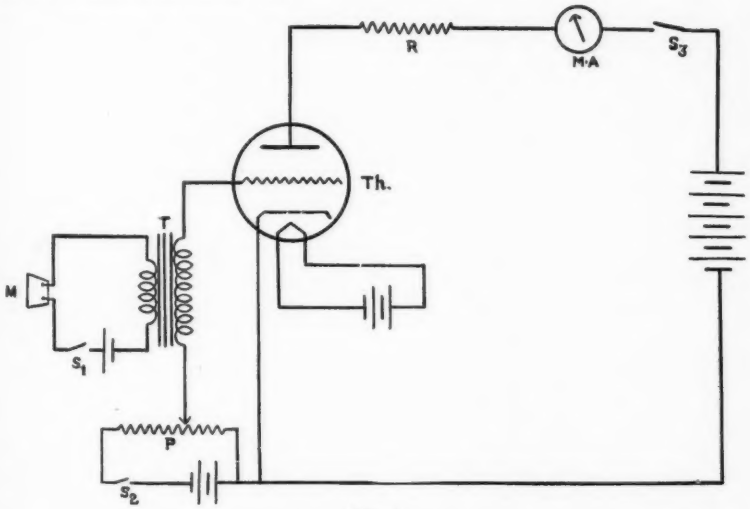

Fig. 1.

Fig. 1 shows the basic circuit of the microphone operated relay. The thyratron Th is connected in series with the load R to be actuated by the

sound phenomena, to a steady source of D.C. voltage. The grid of the thyratron is given a suitable negative bias controlled by the potentiometer P and coupled to a sensitive carbon microphone M through a high ratio step-up transformer T as shown in figure. The negative bias on the grid of the thyratron is adjusted with the potentiometer P so that it is just sufficient to prevent the thyratron from striking and actuating the load circuit when no sound is incident on the microphone. When a sound is incident on the microphone the stepped up alternating potential induced in the secondary of the transformer T momentarily reduces the negative bias on the grid and the thyratron strikes to actuate the load R. By adjusting the static negative bias on the grid of the thyratron it is possible to control the sensitivity of the relay very effectively. For each value of the static negative bias on the grid there is a definite minimum intensity of sound below which the relay will not respond and thus it can be made to operate on any predetermined intensity of sound at a point.

It may be pointed out that the anode and the heater of the thyratron may be supplied with suitable A.C. voltages from a main transformer in which case the grid will regain its control automatically after every response of the relay to the sound phenomena.

The suitability of the said relay as a sound intensity meter to compare the relative intensities of sound at a point was tested as follows. Fig. 1 again shows the electrical connections of the circuit for this purpose. R is now the current limiting resistance to limit the anode current and a milliammeter is included in the circuit to indicate the striking of the thyratron. P is a ten-wire calibrated potentiometer so that the negative bias on the grid can be adjusted and read accurately and the grid is connected to the slider point through the secondary of the step-up high ratio transformer T. The microphone M is of good carbon type and a switch S_1 is included in its circuit. The switch S_3 is included in the anode circuit of the thyratron so

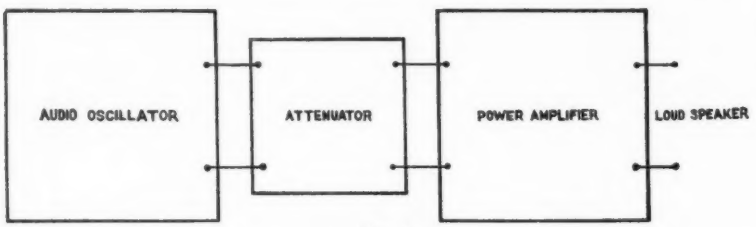

FIG. 2.

that the anode current may be stopped at any time for the grid to regain control. The potentiometer, the anode, the heater of the thyratron and

the microphone are supplied with suitable steady D.C. voltages by storage batteries.

As shown in Fig. 2 the source of sound for this experiment consists of an audio oscillator feeding a power amplifier through an attenuator, the output of the amplifier being fed to a loud-speaker situated at a distance of about 5 feet from the microphone M. The power amplifier consists of a single valve working strictly on the straight line part of its trans-conductance characteristic so that its output power is proportional to the square of the input R.M.S. voltage at the grid ; and this is checked by an output meter substituted in the place of the loud speaker. The exciting voltage to the grid is controlled by the calibrated attenuator and it is easily seen that under the above conditions the intensity of the sound emitted by the loud speaker is proportional to the square of the exciting voltage at the grid of the amplifier.

The switch S_1 is kept open while S_2 and S_3 are closed and the negative bias on the grid of the thyratron is slowly reduced until the thyratron just strikes as indicated by the milliammeter. The reading of the potentiometer just before the striking of the tube is noted and the grid bias required to just prevent striking under silent conditions is obtained. The experiment is repeated with switch S_1 closed and no sound incident on the microphone so that errors due to any back-ground noise, external or internal, is eliminated. It will be generally found that the bias required with the switch S_1 closed is a little more than when it is open. Next the source of sound already mentioned is allowed to emit a note of 1,000 cycles per second at steady intensity and the static grid bias required now is more than that required under silent conditions. Thus the static negative bias on the grid to prevent the thyratron from striking for different intensities of sound of the same frequency emitted by the loud-speaker before the microphone M is found out.

The curve in Fig. 3 is obtained by plotting the relative intensities of the emitted sound in decibels against the respective reading of the potentiometer which is proportional to the static bias on the grid to just prevent the striking. It is easily seen that the curve thus obtained is quite smooth and sensibly linear over a good range of sound intensity. Intensities of sound different from those plotted values were produced and measured with the relay and the above calibration curve. It was found that the relative intensities can be thus determined within 5 per cent. error. The main source of error is due to the variation of the working temperature of the thyratron and the consequent variation in its characteristic. Gaseous triodes filled with argon gas and having low temperature variation characteristic are subject to erratic behaviour, perhaps due to the abrupt variation in the

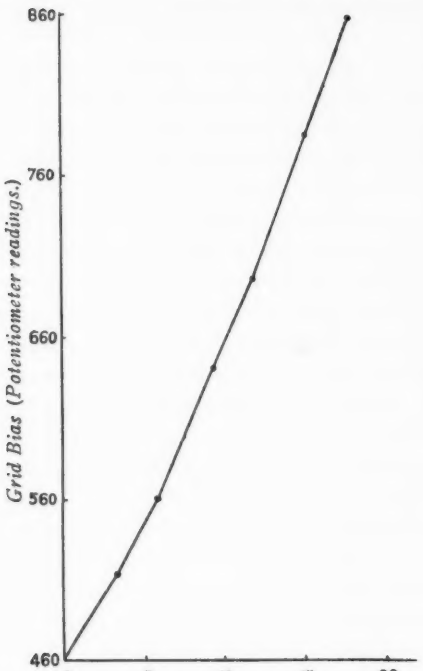

FIG. 3.

internal conditions. By keeping the working temperature of the thyratron constant and using a tube with low temperature variation characteristic quite good results can be obtained. The linearity of the calibration can be improved by using a better quality microphone.

Apart from the use of the relay as a simple sound intensity meter there are other interesting applications of the device. The relay is found suitable for the automatic operation of camera shutters in sound wave-form recording and reliable operation is easily secured. With tuned circuit in the grid of the thyratron the relay can be made to respond to a particular frequency or band of frequencies which may find useful applications in electro-acoustics. Many other useful applications may suggest themselves and in general, wherever any operation or device is to be controlled by a sound phenomena, the relay can be used with successful results.

The above experiments were conducted in the Physics Laboratories of the Presidency College, Madras, and the author's thanks are due to the University of Madras and to Dr. H. P. Waran for all the facilities given to him.

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